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Aquatic Nuisance Species Research Program

pH Pivoting for Algae Coagulation

Bench-Scale Experimentation

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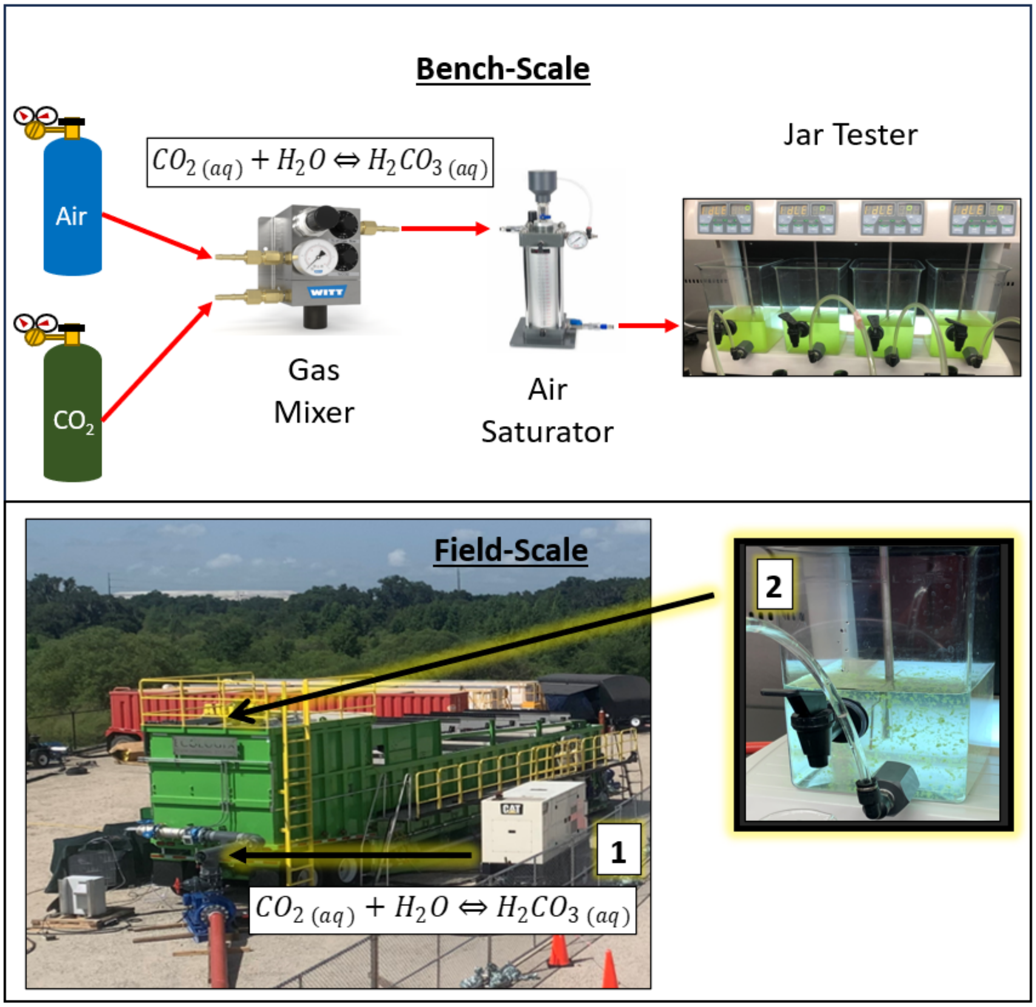
May 2024



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under Project Number 501289; Civil Direct Funding Account Code U4396469

Abstract

Harmful algal blooms (HABs) threaten recreational waters and public supplies across the US, causing detrimental economic and environmental effects to communities. HABs can be mitigated with dissolved air flotation (DAF) treatment, which requires addition of pH-sensitive charged chemicals to neutralize algae, allowing them to attach to microbubbles and float to the surface. During HAB events and photosynthesis, algae raise the pH to levels that are not ideal for DAF. Traditionally, pH is reduced with a strong acid; however, this adds operational cost and permanently adjusts the water's pH. This study assessed an approach that might allow for infusing CO_2 from diesel-powered electricity generators into the water prior to DAF treatment. It was hypothesized that formation of carbonic acid could temporarily reduce the pH. Results showed that 2.5%–5.0% CO_2 mixed within compressed air can achieve pH levels between 6–7 in algal water with an initial pH of 9–11 and alkalinity of 150 mg/L as $CaCO_3$. Further, dosing CO_2 before chemical addition yielded a 31% improvement in water clarification. Returning the pH back to natural levels was not achieved using ambient air microbubbles; however, coarse bubble air spargers should be tested to provide more volumetric capacity for CO_2 absorption.

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Preface

This study was conducted for the US Army Corps of Engineers (USACE) under Aquatic Nuisance Species Research Program (ANSRP), AMSCO Code 008284, under Project Number 501289; Civil Direct Funding Account Code U4396469. Mr. Mike Greer was ANSRP program manager, and Dr. Jennifer Seiter-Moser was technical director, Environmental Engineering and Sciences, Civil Works.

The work was performed by the Emergency and Operational Support Branch of the Operational Science and Engineering Division, US Army Engineer Research and Development Center–Construction Engineering Research Laboratory (ERDC-CERL). At the time of publication, Ms. Ellen Hartman was branch chief; and Dr. George Calfas was division chief. The deputy director of ERDC-CERL was Ms. Michelle Hanson, and the director was Dr. Andrew Nelson.

COL Christian Patterson was commander of ERDC, and Dr. David W. Pittman was the director.

1 Introduction

1.1 Background

In an industrial society, the proliferation of pollutants such as excess nitrogen and phosphorus have the unintended consequence of feeding into the growth of algal colonies in waterways, affecting aquatic ecosystems as a result. Point-source release of phosphorous and nitrogen is not limited to wastewater release from commercial sources; releases from sewage, agriculture, and drainage provide a traceable source of pollutant release that supplement algal growth (Manuel 2014). Non-point-source pollution processes, including runoff, soil erosion, and improperly managed waste discharge provide a difficult to identify, yet crucial source of nutrient dispersal that feed into blooming algal colonies. Harmful algal blooms (HABs) represent these overabundant algal colonies born by the nutrients fed by both point and nonpoint source polluters, providing the colonies with the toxic and biological challenges necessary to overtake local aquatic life (Anderson et al. 2021).

Sustained pollution processes through nutrient excess continues to push the HAB crisis to greater levels. HABs present problems to the aquatic and human domains. HABs demand increased levels of oxygen on an ecosystem; the resulting oxygen depletion along with excess nutrient applications come with the risk of dead zones where marine life becomes incompatible with their local habitat (Diaz and Rosenberg 2008).

The human impact of cyanobacteria HABs come in the form of health and economic consequences. Neurotoxin release in aquatic life can be latent within contaminated species while causing food-born illness in humans (Berdalet et al. 2015). Contamination of seafood in fisheries can lead to shutdowns of contaminated areas in an effort to quarantine HAB spread to unaffected resources (Anderson et al. 2000). HAB exposure and ubiquity create social challenges for public recreation and tourism in communities reliant on aquatic ecosystems. Closures of recreational zones due to extraneous algae concentrations provide a challenge to economies reliant on tourism to relevant aquatic destinations (Bechard 2019).

Eutrophication of poorly drained waterways is increasing, especially within nations that rely on high-intensity agriculture in response to a growing population. As countries strive to provide food resources for a large, dense population; the shift to better drained areas have yet to become a priority, leading to increasing rates of eutrophication-based algae hotspots (Anderson 2012). As algal blooms become an increasing global problem, the challenge has shifted to prevention, mitigation, and treatment to combat the challenges presented by HABs.

1.1.1 The Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS)

The Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS) research project began in 2019 in response to the 2018 Water Resources Development Act (WRDA). The 2018 WRDA authorized the US Army Corps of Engineers (USACE) Engineer Research and Development Center (ERDC) to perform HAB prevention, mitigation, and monitoring research after repeating widespread HAB events at Lake Okeechobee, Florida, that have affected USACE's flood risk management mission and the health of local communities. This effort is led by principal investigator Dr. Martin Page of the ERDC-Construction Engineering Research Laboratory (CERL), with the support of interdisciplinary researchers from CERL, ERDC-Environmental Laboratory (EL), the Pacific Northwest National Laboratory (PNNL), the Illinois Sustainable Technology Center, the University of Illinois at Urbana-Champaign, industry partners, and state governments.

HABITATS intercepts algae-laden water using booms, floating weir skimmers, and suction pumps. The booms help direct the algae to the weir skimmers, which filter out debris with a 3/8 in. screen, and with the aid of the pumps, draw the top foot of water from the source.[1] The algae are separated from the water using dissolved air flotation (DAF) treatment, where coagulants and flocculants are mixed upstream to facilitate coagulation and flocculation (process described in Sections 1.1.2 and 1.1.3), then microbubbles (MBs) are injected at the bottom of the system to float the algae flocs to the water surface, where the flocs are then skimmed off the surface using a mechanical scraper and collected in a hopper. The algae are transported from the hopper to a dewatering press using a conveyor belt where excess water is squeezed out to improve the yields of the final step, biocrude generation. The algae are transformed into

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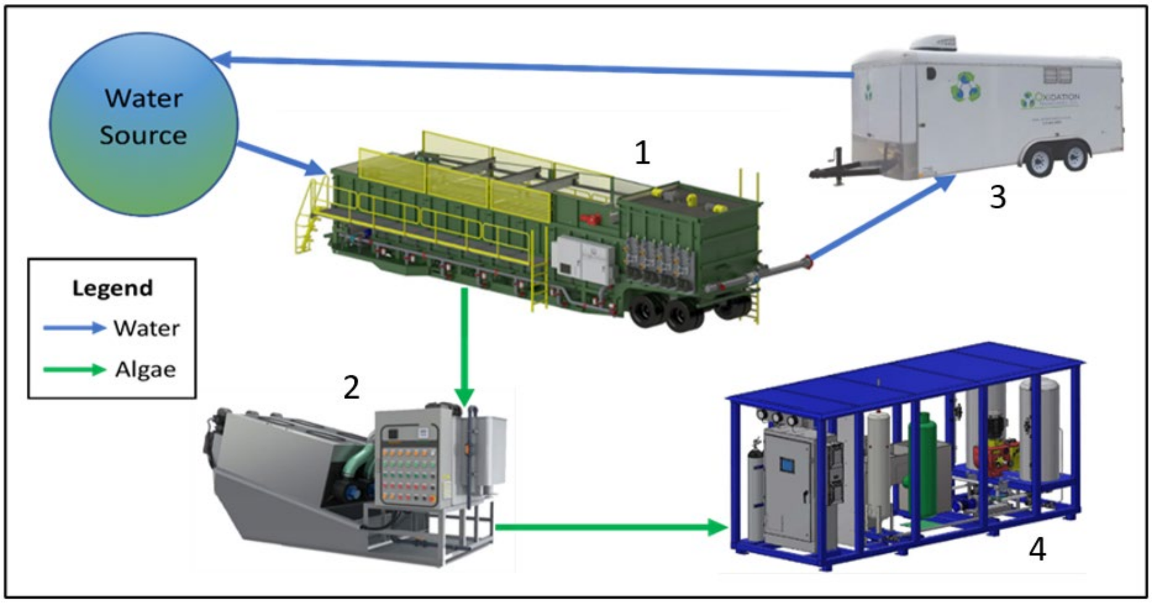
[1] For a full list of the spelled-out forms of the units of measure used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 248–52, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

biocrude via hydrothermal liquefaction technology in only 30 min. Current studies by PNNL are investigating the potential of upgrading this product into a biodiesel that can be used to fuel the HABITATS system, making it a closed-loop process that is energy and cost efficient. The water that was separated from the algae are treated with ozone to eliminate any residual toxins prior to being released back into the water source. A schematic of the HABITATS system is illustrated below in Figure 1. More details of the HABITATS project can be found in the following ERDC technical reports: TR-20-1 (Page et al. 2020) and TR-21-18 (Page et al. 2021).

Figure 1. Flow diagram of the Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS) main components, including the dissolved air flotation (DAF) system (*1*), dewatering press (*2*), ozone generator (*3*), and hydrothermal liquefaction system (*4*).



1.1.2 pH, Coagulation, and Flocculation

Algae are photoautotrophs and take in carbon dioxide from the water during photosynthesis to generate glucose and oxygen. This results in increased pH levels (>9) in the water, and some cyanobacterial species (e.g., *Microcystis* strains) thrive in pH levels as high as 10 (Suter et al. 2024). When CO_2 is consumed, the water pH increases to offset the loss of carbonate species with hydroxide ions.[2] CO_2 replenishment kinetics via Henry's Law, where the concentration of a gas (e.g., CO_2) dissolved in water

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[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.

will equilibrate to a direct proportion of the same gas in the atmosphere (Orenda Technologies 2020), are not able to keep up with the consumption rate. When CO_2 leaves the water, the pH rises due to a reduction in carbonic acid (H_2CO_3) and carbonate ions, which is formed when dissolved CO_2 reacts with water molecules with the stoichiometric equation

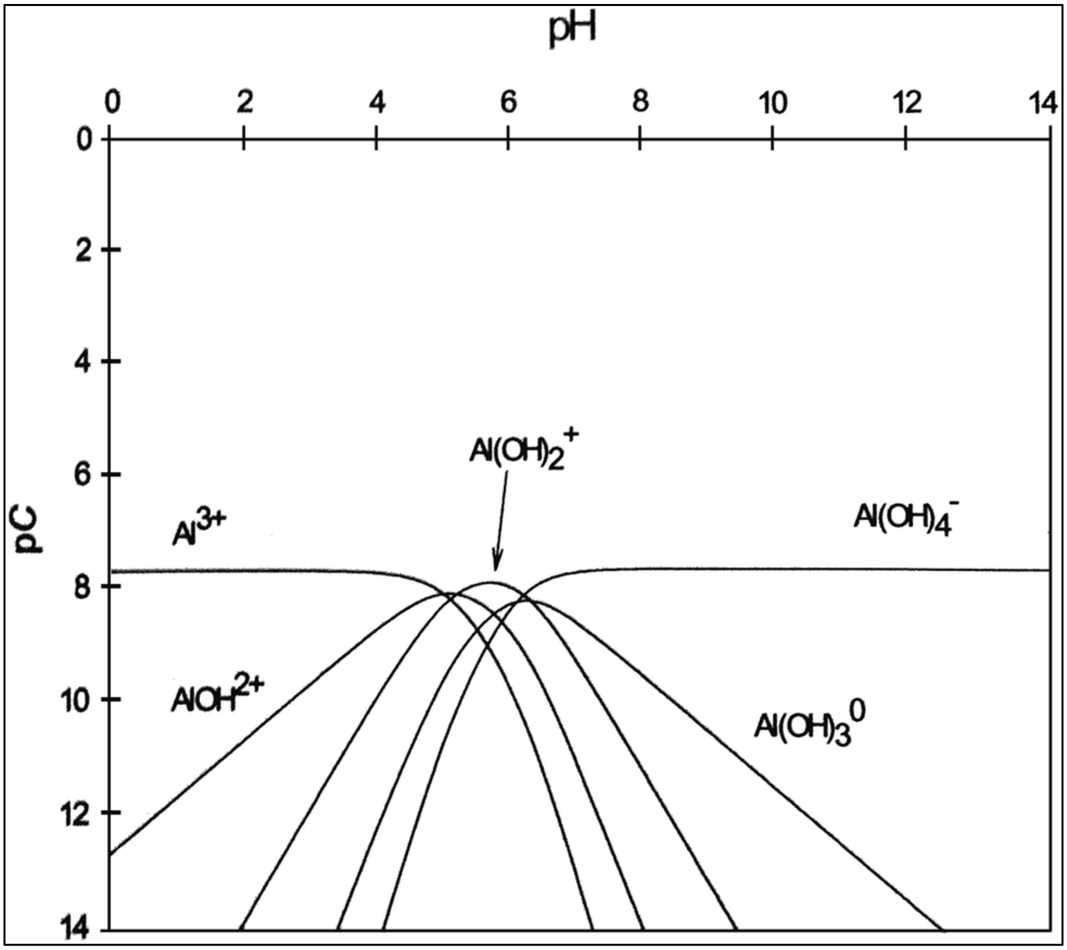
$$\mathrm{CO_{2\,(aq)}} + \mathrm{H_2O} \Leftrightarrow \mathrm{H_2CO_{3\,(aq)}}. \tag{1}$$

High pH levels are typically not ideal for algae coagulation and flocculation. Coagulation is when metal salts or charged polymers (i.e., coagulants) are added to water to neutralize the charge of suspended colloids in water, whereas flocculation is the process of bridging the neutralized cells together. The latter can also be facilitated with the addition of charged long-chain polymers, known as flocculants.

Algal cells have negative zeta potential and are negatively charged because of extracellular polymeric substances or carboxylic and amino functional groups on the cell membrane. This negative zeta potential has an inverse relationship with pH and becomes increasingly negative during the algae's rapid growth stage. The cell membrane is also semipermeable and creates an electric double layer where molecules of positive and negative charges may accumulate on either side of the membrane. (Li et al. 2022). These ions are in an area of dynamic equilibrium as cations repel each other and anions are attracted to the cations. This double layer is compressed when a strong, positively charged coagulant is added to the solution. This mechanism and subsequent charge neutralization allows the algae particles to come together, or coagulate (Ghernaout et al. 2020). Inorganic coagulants (e.g., aluminum and iron salts) demonstrate optimal activity in acidic pH conditions for algal removal (Figure 2), where strong, positively charged species form due to hydrolysis, protonation, or deprotonation of surface groups (Li et al. 2022; Liu et al. 2018).

Inorganic coagulants (e.g., aluminum and iron salts) demonstrate optimal activity in acidic pH conditions for algal removal (Figure 2), where strong, positively charged species form due to hydrolysis, protonation, or deprotonation of surface groups (Li et al. 2022; Liu et al. 2018).

Figure 2. Log concentration of aluminum species across pHs (Liu et al. 2018, Fig. 6, 38814. Used in accordance with the Creative Commons Attribution [CC BY-NC 4.0], https://creativecommons.org/licenses/by-nc/4.0/.)



The traditional method for pH reduction in water treatment is to add a strong acid such as HCl. However, this is not economical at large scales, especially with waters characterized by high alkalinity (thus high acid demand). Nor is it eco-friendly, as sensitive biota may experience increased mortality, decreased growth, and reproductive impacts because of pH fluctuations (Suter et al. 2024). Furthermore, HCl destroys alkalinity when it binds to bicarbonate ions (Orenda Technologies 2020).

1.1.3 Alkalinity

Alkalinity is a water quality parameter which measures how resistant a water is to pH changes via acid neutralization. This is also known as the water's buffering capacity. Total alkalinity is defined as

$$[\text{Total Alkalinity}] = 2\left[CO_3{}^{2-}\right] + [HCO_3{}^{-}] + [OH^{-}] - [H^{+}], \qquad (2)$$

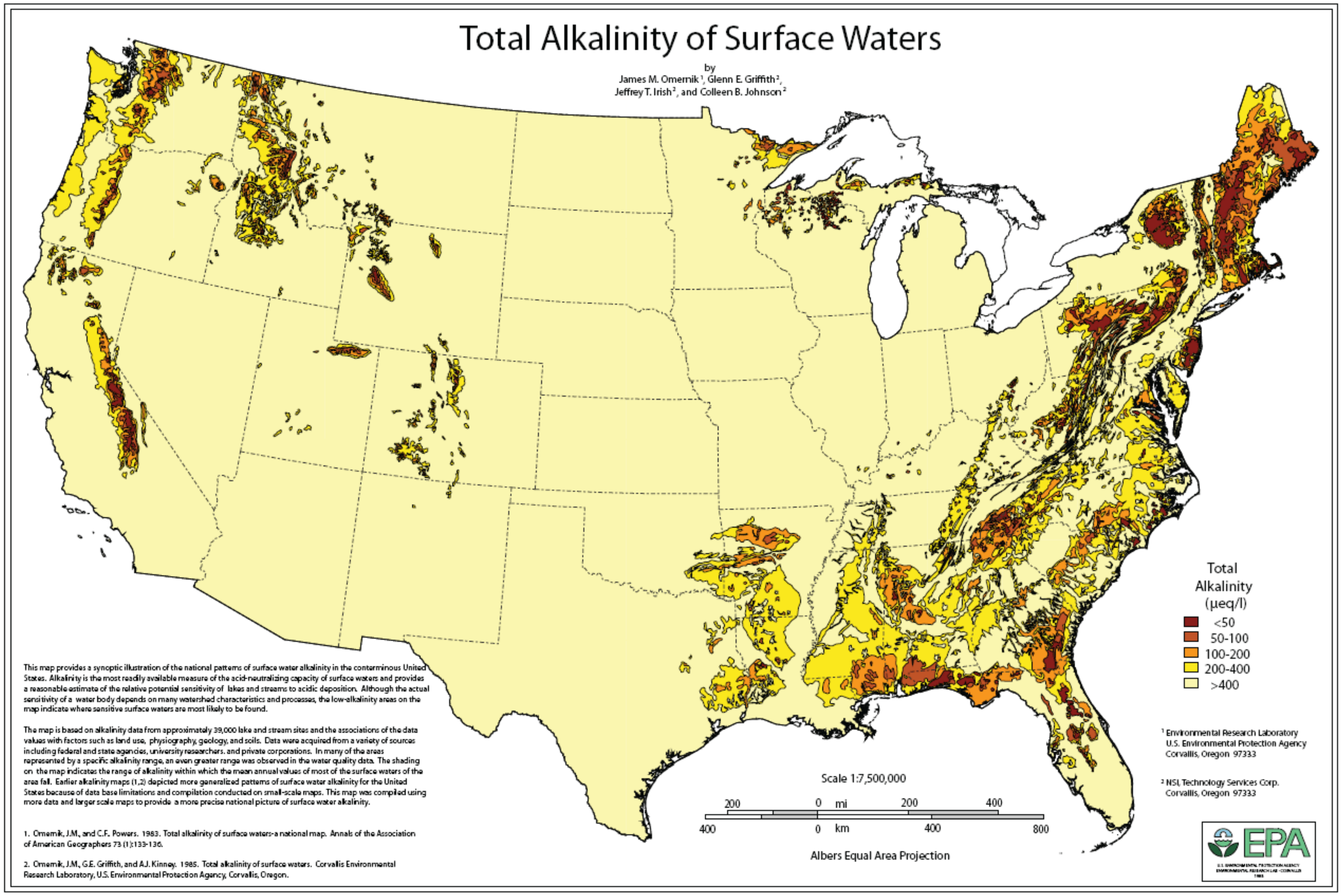
where

$[CO_3^{2-}]$ = carbonate,
$[HCO_3^{-}]$ = bicarbonate,
$[OH^{-}]$ = hydroxyl ions,
$[H^{+}]$ = hydrogen ions, and
[ ] = concentration of ions.

As alkalinity rises, it becomes increasingly difficult to lower the pH (Dunnivant 2004; Water Science School 2018).

According to Figure 3, a map of total alkalinity of surface waters across the continental US developed by the EPA using 39,000 lake and stream sites, most of the country's surface waters have alkalinity levels higher than 400 µeq/L. In Florida, a state that experiences frequent HAB events, there is a variability in alkalinity values (also confirmed in Unsell 2009). In the northwest and central regions of the state, total alkalinity values have been recorded <50 µeq/L and 50–100 µeq/L. Values between 100 µeq/L and 200 µeq/L have been recorded in northern regions, values between 200 µeq/L and 400 µeq/L have been recorded in northern, central, and western regions, and >400 µeq/L have been recorded everywhere in between. Alkalinity depends on the surrounding geology and geography of the land, as precipitation and runoff through the watershed transports chemicals from rocks (i.e., limestone rich in calcium carbonate) to downstream water bodies (Water Science School 2018).

Figure 3. Total alkalinity of surface waters in the continental US. (Image reproduced from J. M. Omernik et al. Public domain.)



This map provides a synoptic illustration of the national patterns of surface water alkalinity in the conterminous United States. Alkalinity is the most readily available measure of the acid-neutralizing capacity of surface waters and provides a reasonable estimate of the relative potential sensitivity of lakes and streams to acidic deposition. Although the actual sensitivity of a water body depends on many watershed characteristics and processes, the low-alkalinity areas on the map indicate where sensitive surface waters are most likely to be found.

The map is based on alkalinity data from approximately 39,000 lake and stream sites and the associations of the data values with factors such as land use, physiography, geology, and soils. Data were acquired from a variety of sources including federal and state agencies, university researchers. and private corporations. In many of the areas represented by a specific alkalinity range, an even greater range was observed in the water quality data. The shading on the map indicates the range of alkalinity within which the mean annual values of most of the surface waters of the area fall. Earlier alkalinity maps (1,2) depicted more generalized patterns of surface water alkalinity for the United States because of data base limitations and compilation conducted on small-scale maps. This map was compiled using more data and larger scale maps to provide a more precise national picture of surface water alkalinity.

1. Omernik, J.M., and C.F. Powers. 1983. Total alkalinity of surface waters-a national map. Annals of the Association of American Geographers 73 (1):133-136.

2. Omernik, J.M., G.E. Griffith, and A.J. Kinney. 1985. Total alkalinity of surface waters. Corvallis Environmental Research Laboratory, U.S. Environmental Protection Agency, Corvallis, Oregon.

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U.S. Environmental Protection Agency
Corvallis, Oregon 97333

[2] NSI, Technology Services Corp.
Corvallis, Oregon 97333

1.1.4 Dissolved Air Flotation (DAF)

DAF involves injecting air bubbles into a solution with the goal of separating target compounds from the bulk solution. DAF is used in a variety of applications such as the separation of oily substances from oil-water emulsions and the harvesting of algae in wastewater oxidation ponds (Saththasivam et al. 2022; Wiley 2009). DAF is effective at separating small, suspended particles from solution, encouraging the formation of larger algae flocs, and has been recognized as being an efficient and cost-effective way to harvest algae (Wiley 2009; Xu et al. 2010). DAF is often used with the addition of coagulants and flocculants to destabilize suspended particles and enhance the separation of the target compound. Saththasivam et al. (2022) report that some of the shortcomings of DAF are the sometimes high required doses of coagulants, the need for pH adjustments to the water, and the presence of potentially harmful coagulant residues in effluent waters.

In HABITATS, DAF is used to inject compressed air (CA) MBs into algae-laden water for treatment. MBs are bubbles with a diameter of less than 50 µm (Takahashi 2005). Because of their small size, MBs have high surface tension, low buoyancy, and increased mass-transfer capabilities (Bang, et al. 2014; Takahashi 2005). Their low buoyancy means they rise slowly through a solution, increasing the contact time between the gas-liquid interface. Additionally, their high surface tension results in MBs not popping easily, and remaining on the surface of the solution for extended periods of time.

As described above in Section 1.1.3, dissolved CO_2 affects the pH of the solution. The solubility of a gas in a solution is dictated by Henry’s Law, with factors like temperature and pressure influencing how much of the gas can be expected to dissolve into the liquid (Bang et al. 2014). The unique characteristics of MBs also enhance the solubility of carbon dioxide in solutions. Bang et al. (2014) reported that carbon dioxide MBs (99.9% purity) were able to lower the pH of a range of $CaSO_4 \cdot 2H_2O$ solutions from around 12 to between 8 and 6. Furthermore, in 2014, Kim and Kwak (2014) developed a single-collector model for simulating algae removal with carbon dioxide bubbles. They concluded that optimal collision-attachment efficiency between carbon dioxide and algae occurs under the following conditions: similar sizes of MBs and algae, and high algae density and positive zeta potential, as opposed to negative bubble zeta potential (Kim and Kwak 2014).

1.2 Objective

The objective of this research was to test the hypothesis that a reduction in the water's pH via CO_2 infusion will improve the ability of water treatment chemicals to facilitate coagulation and flocculation of algal cells, improving the separation process of the biomass from the water. This hypothesis was tested at bench-scale.

1.3 Approach

Bench-scale experimentation was executed through jar tests modified with air saturation to simulate the HABITATS DAF technology that separates algae from water. Lab-cultivated algae were used in the jar tests, where a single parameter is isolated and optimized for each test, then held constant in succeeding experiments. The parameters chosen include alkalinity, pH, chemical doses, ratio of ambient CA to CO_2 MBs to achieve the targeted pH, and algae density. CO_2 stripping using ambient air MBs to reequilibrate pH levels was investigated as well. All experiments were performed in duplicate or triplicate, depending on time and resource constraints. Furthermore, all experiment matrices were completed with either CO_2 MBs or ambient CA MBs for direct comparison to evaluate whether CO_2 MBs demonstrated a significant impact on chemical performance.

2 Materials and Methods

2.1 Algae Cultivation

Algae were cultivated in sterilized glass jars using the University of Texas (UTEX) BG-11 growth media recipe (UTEX, n.d.). The BG-11 formulation can be referenced in the Appendix. The vessels were seeded with mixed algal cultures from a pool growing outside CERL in Champaign, Illinois since 2021. This pool of algae originated with samples from Lake of the Woods in Mahomet, Illinois. Each carboy was continuously stirred at 130 rpm on a stir plate with air pumped into it via an aeration stone, which was submerged at a depth equidistant from the water surface and bottom. To simulate natural photoperiods and facilitate photosynthesis, growth lights (Figure 4) were set to be cycled on for 12 hr/day. The algae used in experimentation was replaced with an equal volume of deionized (DI) water. For every liter replaced, one milliliter of BG-11 was added to encourage new algal growth.

Figure 4. Algae cultivation setup with growth lights off (*left*) and on (*right*).

2.2 Alkalinity Titration

Baseline alkalinities of the algae cultures were measured with a pH meter titration method (Dunnivant 2004), where curves such as Figure 5 were generated as a function of pH and volume of 0.2 mol/L HCl added. The alkalinity at the equivalence point (pH 4.5) was calculated by inputting volume of HCl added and the following equations:

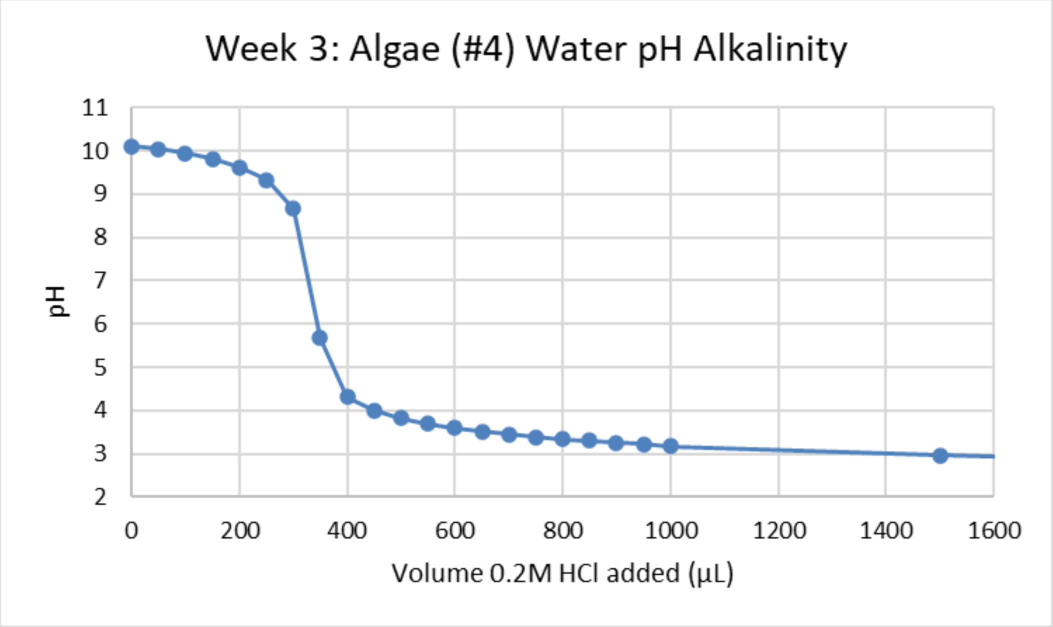
$$(\text{Vol. of acid used})(\text{Molarity of acid}) = \text{Moles of acid used}, \tag{3}$$

$$\frac{(\text{Moles of acid used})}{(\text{L base solution})}\frac{(1\ \text{equiv.}\ H^{+})}{(\text{Moles of acid})}\frac{(1\ \text{equiv. alk})}{(1\ \text{equiv.}\ H^{+})} = \frac{\text{equiv. alk}}{\text{L}}, \text{ and} \tag{4}$$

$$\frac{(\text{equiv. alk})}{\text{L}}\frac{(1\ \text{equiv. CaCO}_3)}{(1\ \text{equiv. alk})}\frac{(1\ \text{mol CaCO}_3)}{(2\ \text{equiv.CaCO}_3)}\frac{(10^5\text{mg CaCO}_3)}{(1\ \text{mol CaCO}_3)} = \frac{\text{mg}}{\text{L}}\text{as CaCO}_3. \tag{5}$$

The measured alkalinity of the 250 mL lab grown algal samples ranged between 10–20 mg/L as $CaCO_3$.

Figure 5. pH titration curve of a lab-cultivated algae sample.



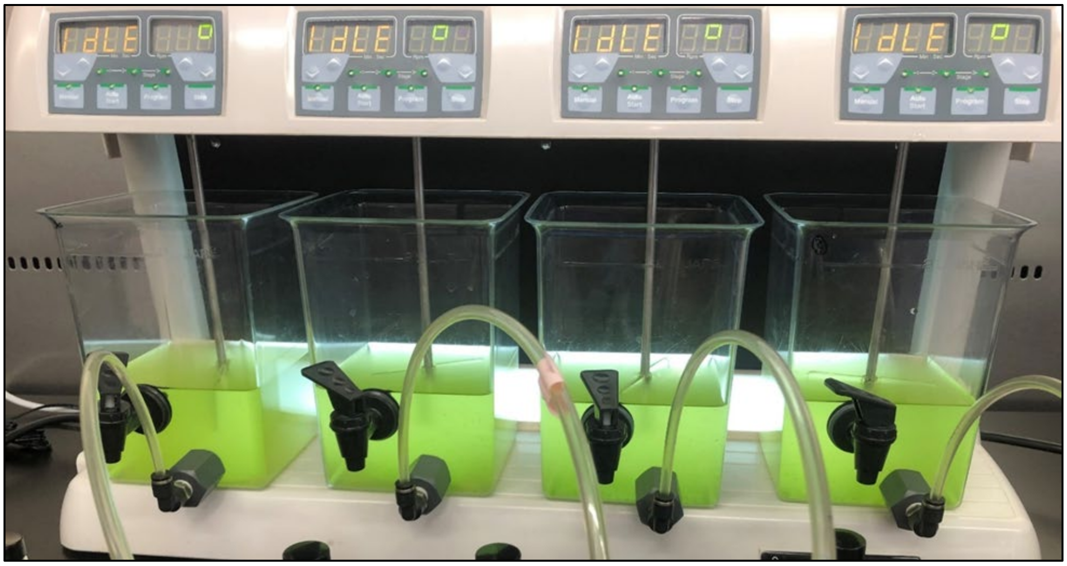
2.3 Jar Testing

2.3.1 Blank Jar Tests

All jar tests were conducted with a four-station programmable Microfloc Platypus Jar Tester (Figure 6). Each jar was filled with 1 L of DI or algal water for the trials. Coagulants were dosed at the start of the first interval of mixing. Coagulants used in this study mirrored those used in previous HABITATS field research demonstrations. DAF MBs were supplied by a Platypus DAF Saturator assembly at 70–75 psi. The assembly consisted of a

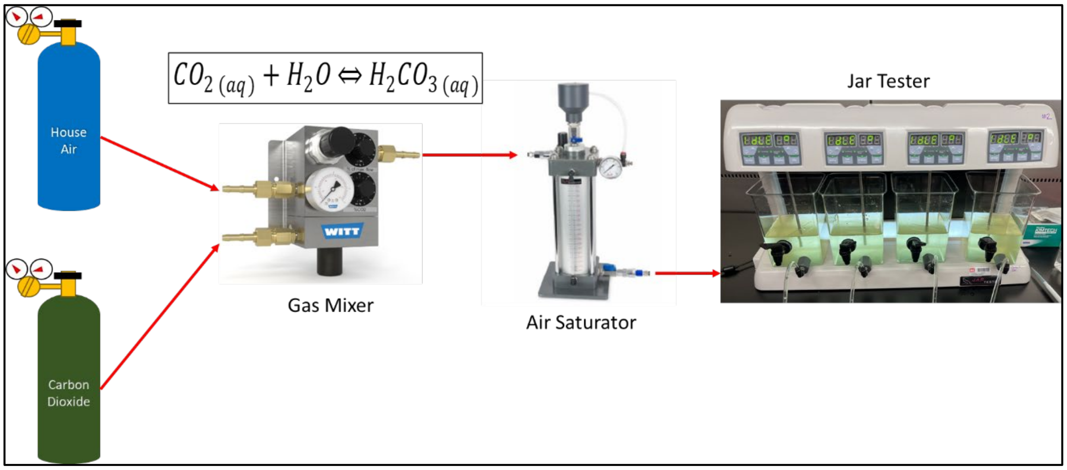
4-port distribution tubing system connected to the jars. Each experiment used one port at a time to prevent reduced air pressure across the manifold.

Figure 6. Close-up view of jar test reactors full of healthy algae before jar testing.



Dissolved CO_2 MBs were supplied by a compressed industrial CO_2 cylinder. A system was constructed to manually switch hoses from the CO_2 tank to CA source and vice versa. The system was also constructed to allow both CA and CO_2 to be connected to the gas mixer and the DAF saturator (Figure 7).

Figure 7. Conceptual design for bench-scale CO_2-enhanced DAF jar testing.



A total of 42 trials were conducted for both DI and algal water (84 total trials) to observe change in pH due to 100% CA MBs or 100% CO_2 MBs. Seven tests of varying MB volumes (50–600 mL) were conducted and repeated in triplicate, where either CA or CO_2 was used to inject MBs into either 1 L of DI or algal water. These preliminary trials were conducted to confirm whether CO_2 induced a significant decrease in pH compared to CA.

2.3.2 Enhanced Alkalinity Jar Tests

A total of 32 jar test trials were conducted with alkalinity enhanced DI and algal water to observe the change in pH, using either 100% CA or 100% CO2 MBs, as a function of alkalinity. The test water volume was fixed at 1 L for this experiment and all succeeding jar test experiments. Alkalinity was added using sodium bicarbonate ($NaHCO_3$) and converted to standard units as $CaCO_3$. Alkalinity values from 0–100 mg/L were tested. The volume of MBs added was 200 mL.

2.3.3 Mixed Gas: Microbubbles (MBs) Only

To fine tune to targeted pH levels in algae-laden water, experiments were designed using the Witt MM-Flex gas mixer that mixes CO_2 and CA. The mixer can be fixed at ratios between 0% and 100% and is graduated at 5% increments. 11 jar tests were conducted with 200 mL of MBs of varying ratios (CA:CO_2), including 100:0, 75:25, 50:50, 25:75, 0:100, and 95:5. Figure 8 illustrates the jar tester set up with the gas mixer assembly.

Figure 8. Physical experiment set-up for bench-scale CO_2-enhanced DAF jar testing.

2.3.4 Optimal pH for Greenfloc 5100 (GFT 5100)

Seven experiments were designed to identify the pH required to promote optimal flocculation with a constant concentration of Greenfloc 5100 (GFT 5100) at 10 ppm, a cationic starch. For the coagulation and flocculation efficiency trials, the agitation (mixing) program was set to 75 rpm for 30 s for rapid mixing followed by 35 rpm for 2 min for slow mixing. The GFT 5100 was added during the rapid mixing step. The MB parameters were held constant using 200 mL of 100% CA bubbles. pH was adjusted using HCl. Turbidity was measured using the Hach 2100Q turbidimeter. The corresponding pH value to the greatest turbidity change indicated the optimal pH level to achieve the most effective coagulation.

2.3.5 pH as a Function of CO_2 Dose and Alkalinity

Six jar tests were conducted to identify a CO_2 ratio and environmentally relevant alkalinity level that will get our algae water to the desired pH (6–7) identified in the previous GFT 5100 experiments. Jar tests were conducted with and without alkalinity added (0 mg/L, 150 mg/L, or 300 mg/L as $CaCO_3$). Gas ratios tested (CA:CO_2) include 95:5 and 97.5:2.5, where 200 mL volume of MBs were added to the jars.

To mimic the alkalinity levels of natural freshwaters in Florida and reach desired pH levels, succeeding jar test reactors were spiked with 252 mg of sodium bicarbonate to reach a final concentration of approximately 150 mg/L as $CaCO_3$.

2.3.6 Mixed Gas: MBs + Aluminum Chlorohydrate (ACH)

The purpose of these experiments is to investigate the effect of various concentrations of aluminum chlorohydrate (ACH) on algae coagulation. ACH is known to work at a range of pH values, so the pH value optimal for GFT 5100 was used for the succeeding experiments. Thirty-two jar tests with 150 mg/L as $CaCO_3$ added alkalinity, 200 mL of 97.5:2.5 MBs, and ranging concentrations of ACH (0 ppm, 10 ppm, 20 ppm, and 40 ppm) added in the rapid mixing stage were conducted.

2.3.7 Mixed Gas: MBs + GFT 5100

The purpose of these experiments is to investigate the effect of various concentrations of GFT 5100 on algae coagulation. Thirty-two jar tests with 150 mg/L as $CaCO_3$ added alkalinity, 200 mL of 97.5:2.5 MBs, and ranging concentrations of GFT 5100 (0 ppm, 20 ppm, 25 ppm, and 30 ppm) added in the rapid mixing stage were conducted.

2.3.8 Mixed Gas: MBs + GFT 5100 + ACH

The same constant parameters were set as the previous jar tests with either ACH only or GFT 5100, but this time both ACH and GFT 5100 were added in combination simultaneously during the rapid mix stage to investigate the effect of the coagulant doses on algae coagulation. ACH:GFT 5100 ratios tested include 4:4, 4:5, 5:0, 5:2, 5:4, 5:5, 5:6, 5:10, 5:20, 5:25, 10:5, 10:10, 10:20, 10:25. 2:5, 2:10, 2:15, 2:20, 0.5:0, 0.5:1, 0.5:2, and 0.5:3 for a total of 88 jar tests.

2.3.9 CO_2 Before Chemical Addition

The order of CO_2 addition may impact coagulation performance. Unlike the previous experiments, 50 mL of 5% CO_2 was added prior to coagulant addition and mixing to reduce pH beforehand. After coagulant addition, 150 mL of 100% CA was added to the water to float the flocs. Besides the MBs, the other experimental variables remained the same as the previous jar tests (e.g., 1 L of algal water and 150 mg/L as $CaCO_3$ added alkalinity). ACH:GFT doses tested include 5:1, 5:2, 5:4, 5:6, 4:3, and 4:5 ppm ratios.

2.3.10 Algae Density

Eight jar tests were conducted to investigate the effect of constant ACH+GFT 5100 doses on varying concentrations of algae density. A serial dilution of alkalinity enhanced (150 mg/L as $CaCO_3$) 1 L algae jars were made from 100% down to approximately 25% concentrations. Before chemical addition, 50 mL of 5% CO_2 MBs were dosed in the jars to lower the pH. The ACH: GFT 5100 ratio added during the rapid mix stage was 5:4 ppm or 5:6 ppm, and on completion of slow mixing, 150 mL of 100% CA MBs were added.

2.3.11 CO_2 Stripping

To minimize environmental impacts of pH modulation, the possibility of CO_2 stripping, or returning pH levels back to initial conditions, was investigated using 100% CA MBs. Two different approaches were taken to attempt CO_2 stripping:

1. Ten jar tests (5 with alkalinity added, and 5 without added alkalinity) where 200 mL of 2.5% CO_2 bubbles were added, followed by a secondary treatment with varying volumes of 100% CA MBs (0–800 mL). pH was measured immediately after the CA MBs rose to the water surface.
2. Four jar tests (with alkalinity added), where 200 mL of 2.5% CO_2 bubbles were added, followed by a secondary treatment with varying volumes of 100% CA MBs (400 mL or 800 mL). pH was measured over time (0–240 min.) to assess how long it would take for the pH to return back to its original condition.

3 Results and Discussion

All of the experimental data is published on Mendeley Data and can be accessed with the following link: https://data.mendeley.com/datasets/dp3zs5s2rn/1.

3.1 Blank Jar Tests

The blank jar tests were performed to assess whether the CO_2 MBs can immediately reduce the DI and algal water's pH after addition, and to determine the extent of pH reduction as a function of dosage. Figure 9, Figure 10, and Figure 11 demonstrate that even a small amount of CO_2 MBs can drastically lower the pH (3.9–5), with diminishing returns as the dose increases. This can be explained by the CO_2 approaching saturation in the water. A slight decrease in pH is observed in the 100% CA MB trials. This may be because our atmosphere is made up of approximately 0.035% CO_2 (NOAA 2023). Algal water contains more alkalinity by observing the downward slope of the pH between 50 mL and 300 mL of MBs. The slope is far less prominent in the DI water.

Figure 9. Sample data demonstrating change in pH before and after the addition of compressed air (CA) and CO_2 microbubbles (MBs) in deionized (DI) and algae water.

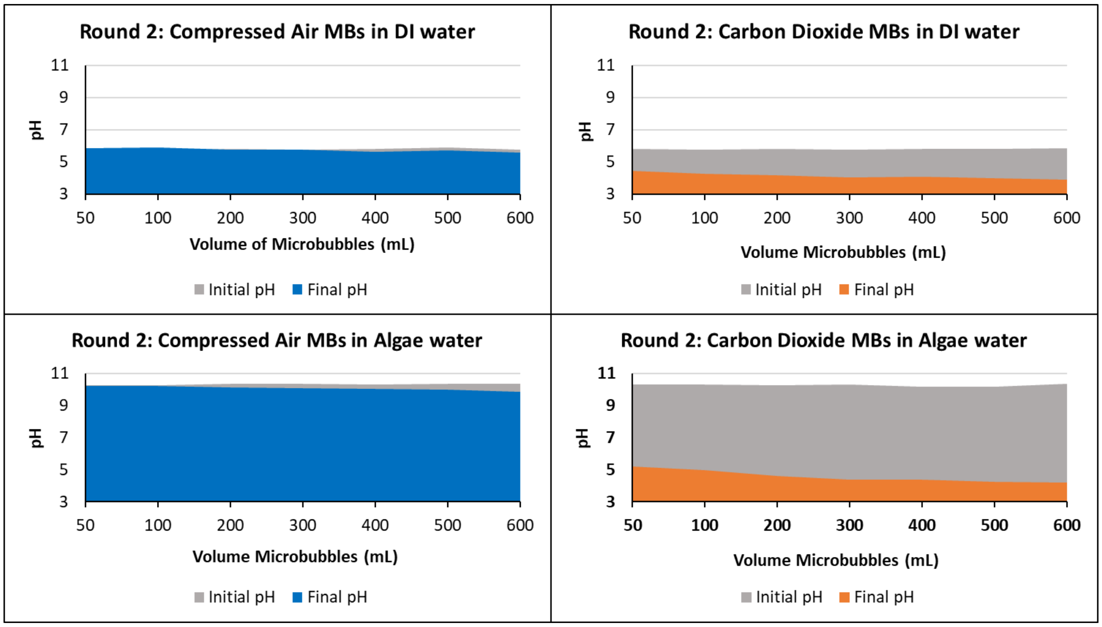


Figure 10. Triplicate results of pH impacts after the addition of CA and CO_2 MBs in DI water.

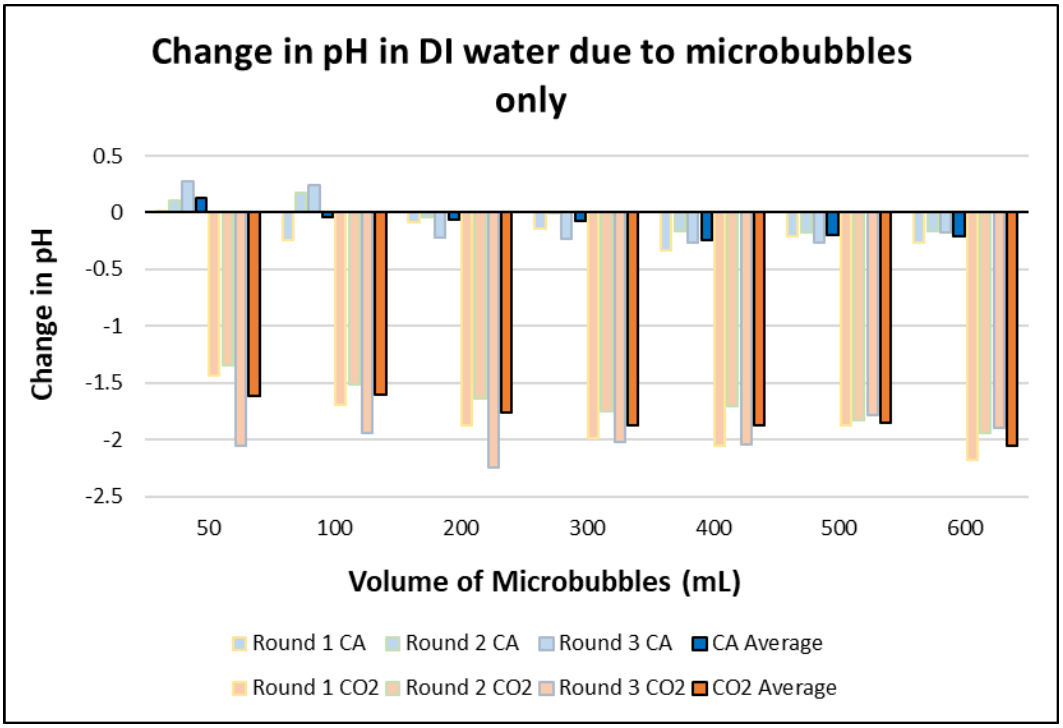
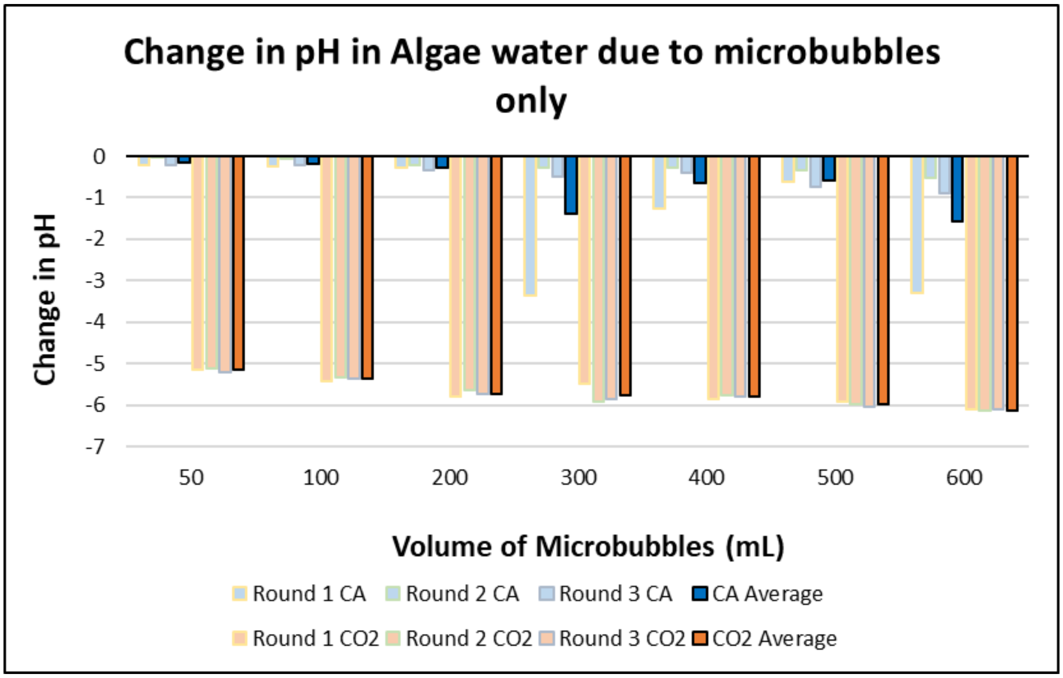


Figure 11. Triplicate results of pH impacts after the addition of CA and CO_2 MBs in algae water.



3.2 Enhanced Alkalinity Jar Tests

In the blank jar tests, significant pH modulation was possible with doses as small as 50 mL of pure CO_2. pH values of 3.9–5 seen in the blank jar test are in a hazardous range for wildlife and are much below our target of 6–7. Therefore, trials were performed with added alkalinity to see if the degree of pH modulation can be reduced. Figure 12 and Figure 13 clearly demonstrate that added alkalinity can reduce the amount of pH modulation in algae water. Because the pH started at a smaller value at 0 added alkalinity, the results show a smaller change in pH initially. After alkalinity was added, the initial pH rose and allowed for a greater drop until saturation was reached. However, the same was not observed in the DI water (Figure 14). Perhaps it's because it started with nearly 0 alkalinity and required more to buffer the CO_2.

Figure 12. Sample data demonstrating the change in pH before and after the addition of CA and CO_2 MBs in alkalinity-enhanced DI and algae water.

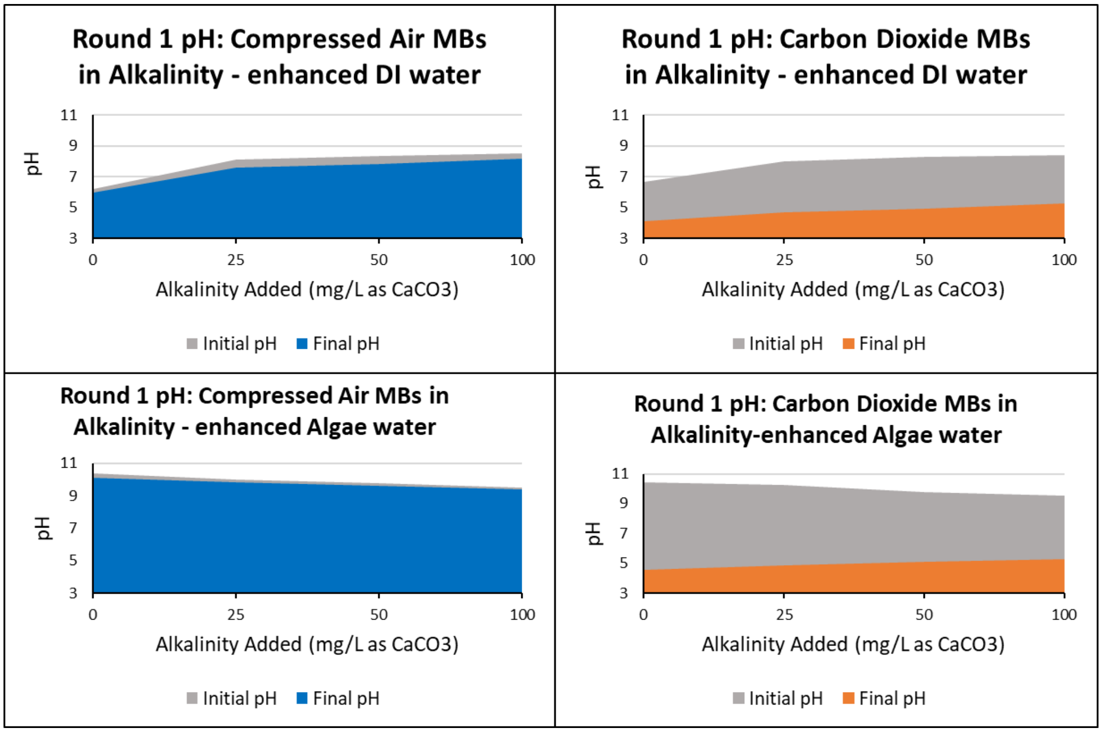


Figure 13. Duplicate results of pH impacts after the addition of CA and CO_2 MBs in algae water.

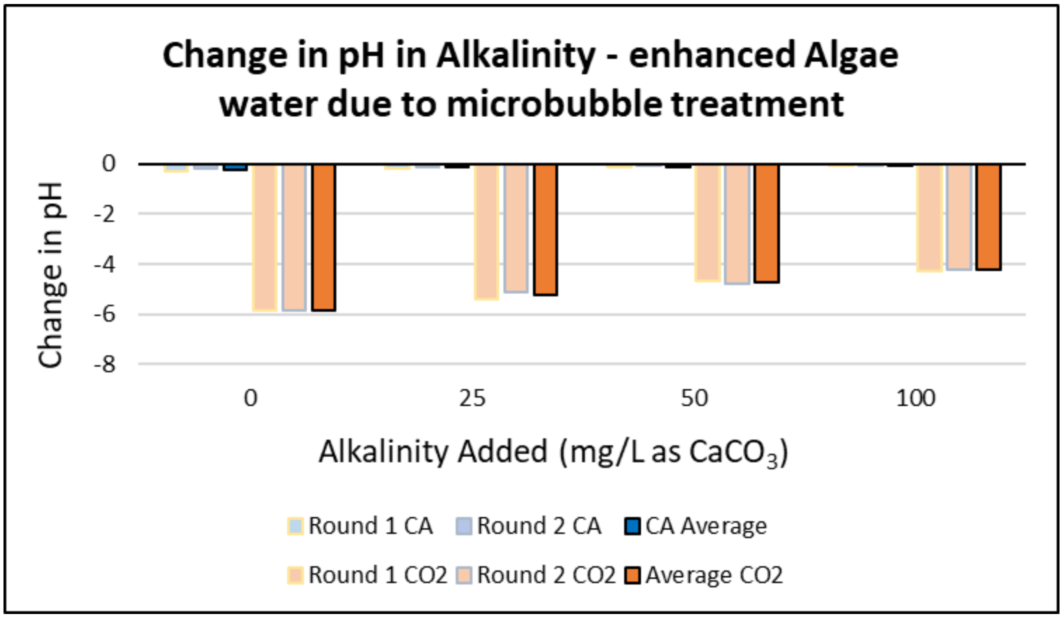
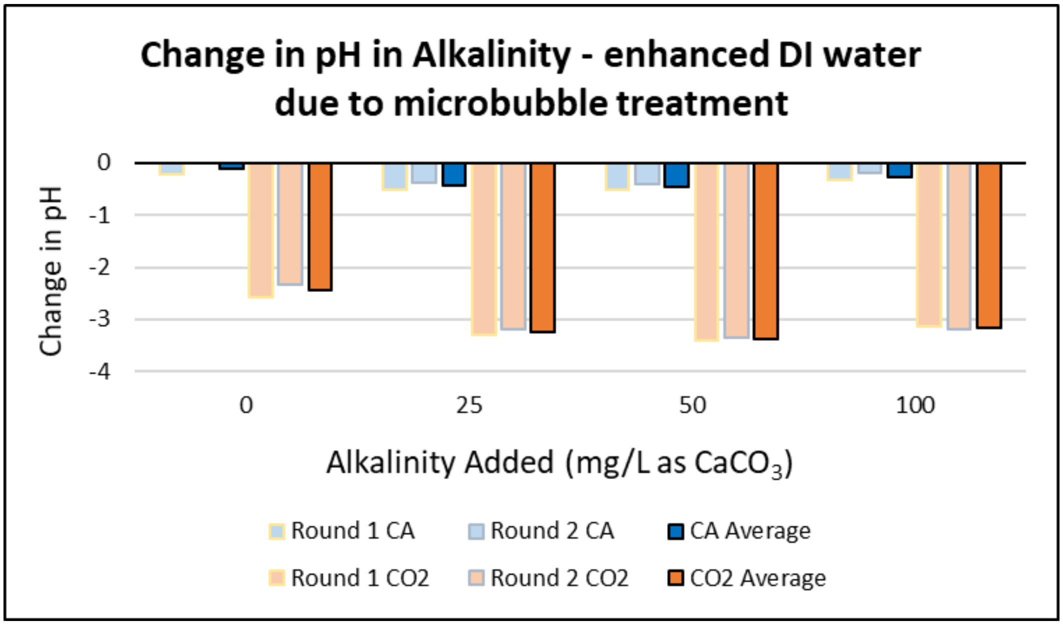


Figure 14. Duplicate results of pH impacts after the addition of CA and CO_2 MBs in DI water.



3.3 Mixed Gas: MBs Only

The pH modulation was still too high in the alkalinity-enhanced jar tests, so it was determined that the CO_2 must be diluted with CA to achieve the optimal pH in algae-laden water. The gas mixer had gradation marks in increments of 5s, so the lowest CO_2 ratio tested was 5%. Similar pH magnitudes were observed with a range of CA:CO_2 ratio doses and are shown Figure 15 and Figure 16, with pH drops hovering around 5 units.

The final pH values ranged from 4.61 to 5.57 with added CO_2 MBs, which are still lower than the ideal range of 6–7. However, the 5.57 value with 5% CO_2 is closer to the ideal range than 100% CO_2.

Figure 15. Average change in pH after the addition of different ratios of a mixture of CA and CO_2 MBs.

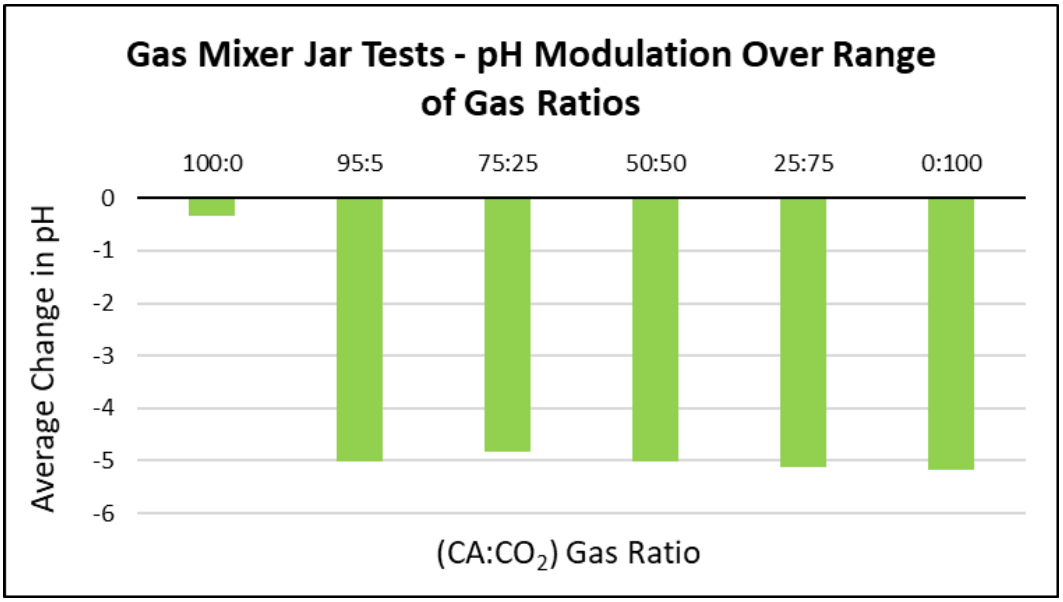
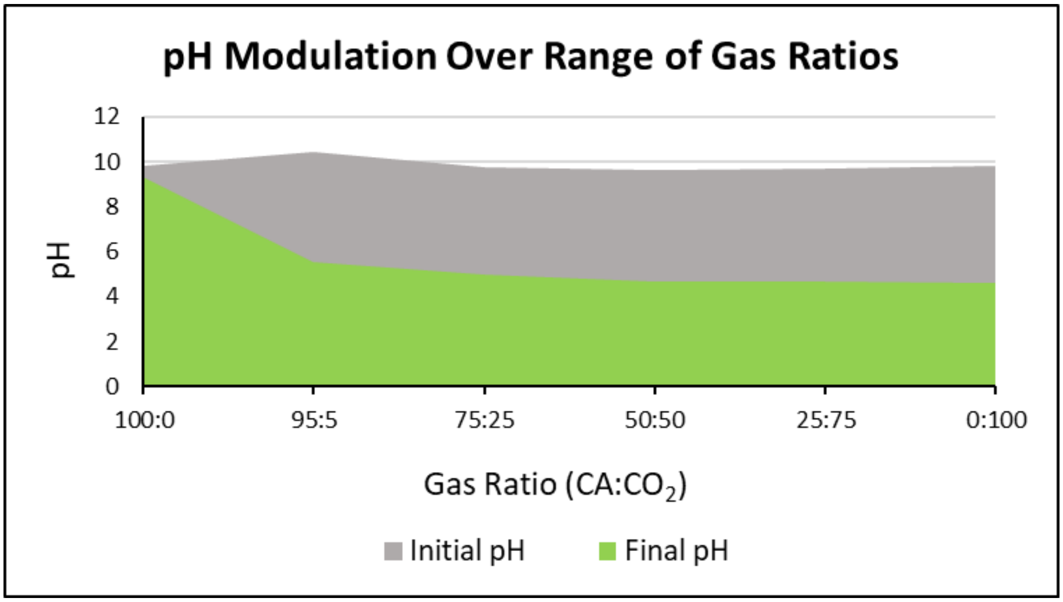


Figure 16. Starting and ending pH values after the addition of different ratios of a mixture of CA and CO_2 MBs.



3.4 Optimal pH for GFT 5100

To verify the target pH range, jar tests were performed with a constant dose of GFT 5100 across a range of pH values. HCl instead of CO_2 was used to lower the pH in the experiment, because the pH drop was more predictable and easier to home in the trial's designed pH. Turbidity was chosen as the metric to determine the effectiveness of the coagulant with respect to pH, because a lower turbidity indicates suspended solid removal (e.g., algae). The highest turbidity reductions were observed between pH values of 6 and 7 as predicted (Figure 17 and Figure 18).

Figure 17. Starting and ending turbidity values after performing jar tests with a fixed dose of GFT 5100 and varying pH values.

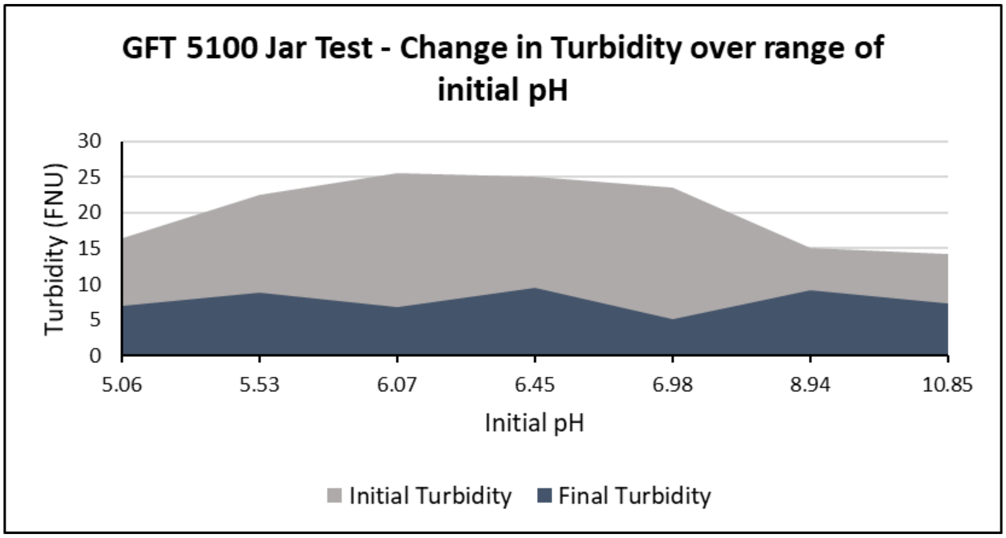
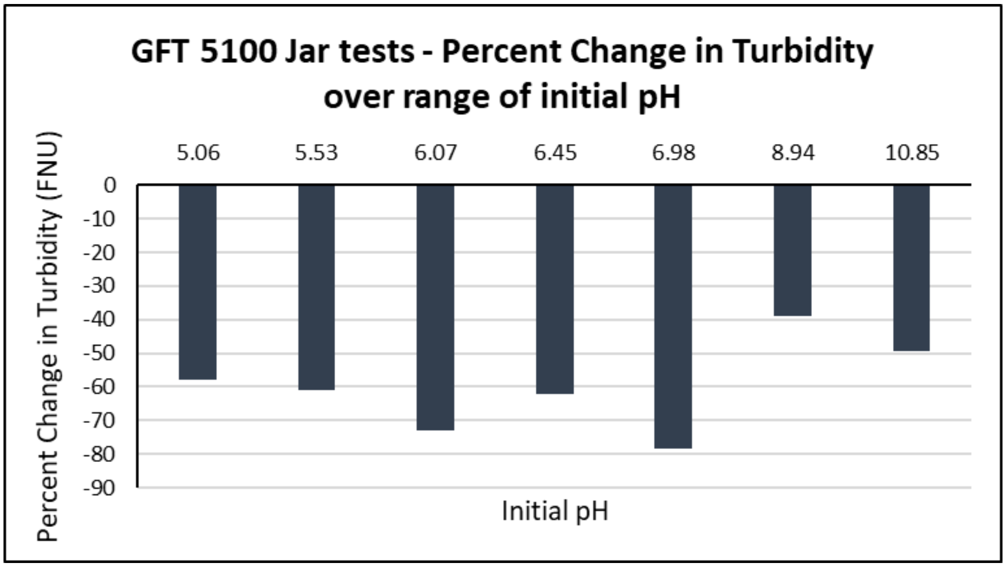


Figure 18. Percent change in turbidity values after performing jar tests with a fixed dose of GFT 5100 and varying pH values.



3.5 pH as a Function of CO_2 Dose and Alkalinity

Further tests were conducted to see if a higher dose of alkalinity, up to 300 mg/L as $CaCO_3$, and a lower dose of CO_2, 2.5%, can lead to achieving the optimal pH for GFT 5100 coagulation. In Figure 19, with 5% added CO_2, a final pH of 6.01 and 6.69 were reached for added alkalinities of 150 mg/L and 300 mg/L of $CaCO_3$, respectively.

When 2.5% CO_2 MBs were added, pH values achieved with added alkalinities of 150 mg/L and 300 mg/L of $CaCO_3$ were 6.29 and 6.22, respectively (Figure 20).

There did not appear to be significant differences with the 2.5% or 5% volumes of CO_2 MBs added, as illustrated in Figure 21. However, both gas ratios experienced a smaller change in pH as alkalinity increased. In conclusion, results within the targeted pH range of 6–7 were achieved.

Figure 19. Starting and ending pH values after the addition of a mixture of CA and CO_2 MBs (95:5) to algae water with varying levels of alkalinity.

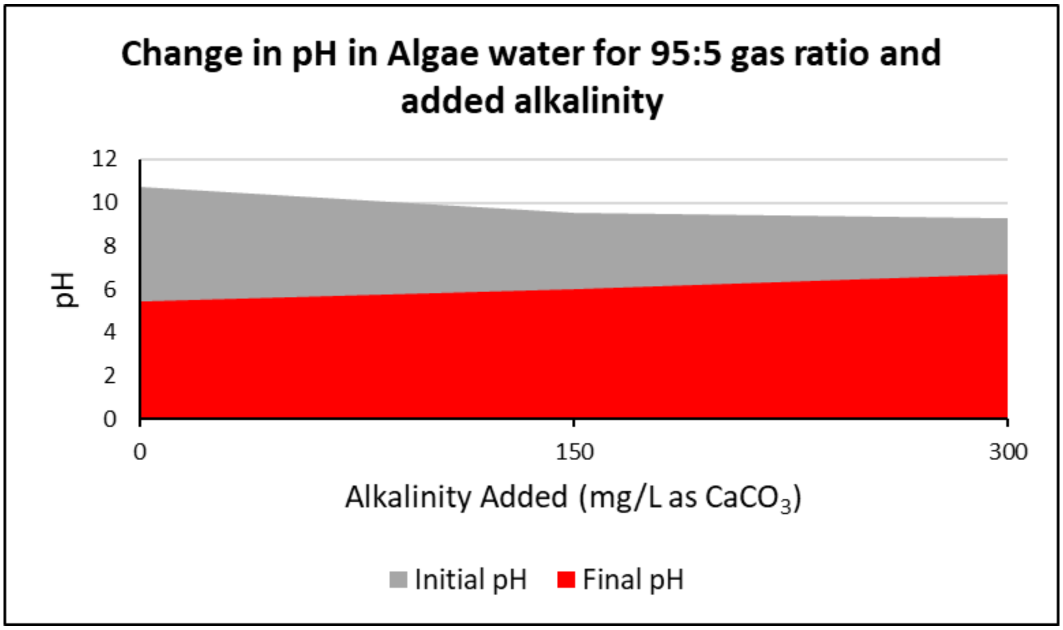


Figure 20. Starting and ending pH values after the addition of a mixture of CA and CO_2 MBs (97.5:2.5) to algae water with varying levels of alkalinity.

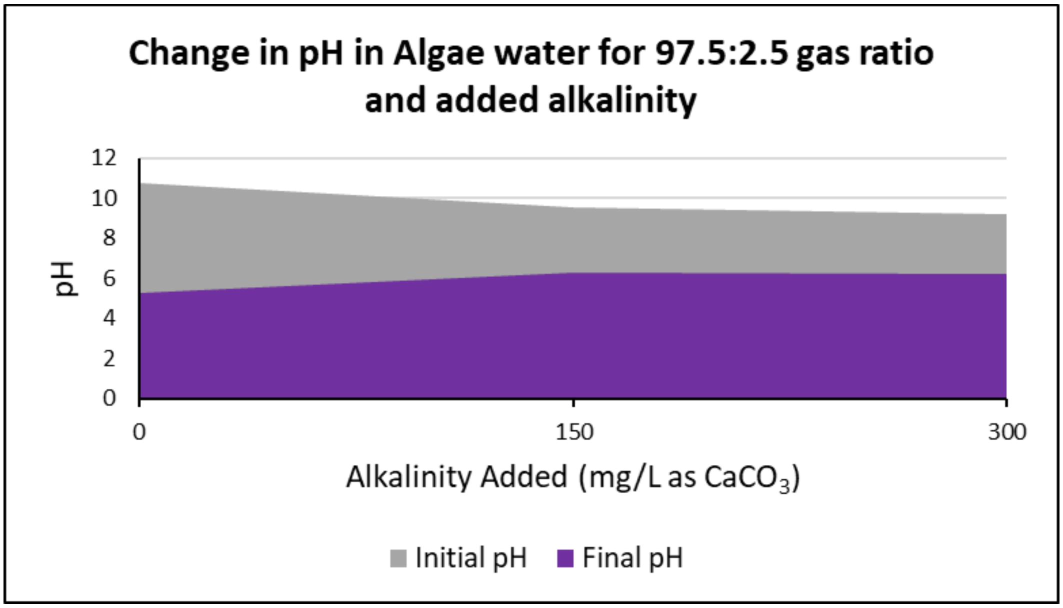
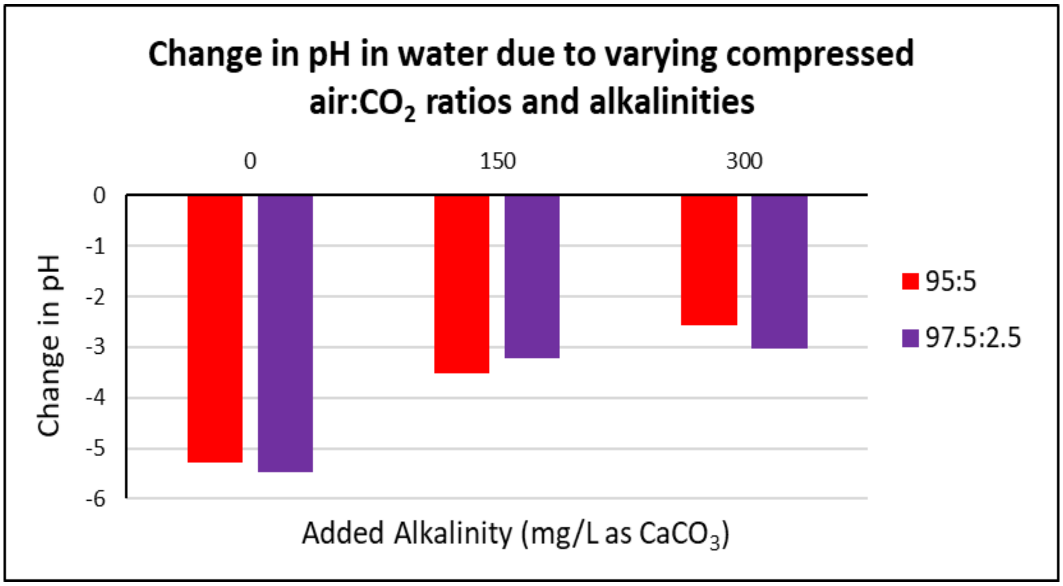


Figure 21. Comparison of change in pH values for trials with varied alkalinity levels and gas mixture ratios.



3.6 Mixed Gas: MBs + ACH or GFT 5100

After achieving the ideal pH range, the next goal was to find ideal doses for the coagulants, ACH and GFT 5100. The coagulants were tested individually in the jar tests. The optimal dose for GFT 5100 for the algal water with turbidities between 16–18 Formazin Nephelometric Units (FNU) appeared to be around 10 ppm (Figure 22 and Figure 23).

For ACH by itself, 20 ppm seemed to be the optimal dose (Figure 23 and Figure 24). However, there didn't appear to be significant differences in the 100% CA or 2.5% CO_2 trials.

Figure 22. Sample data demonstrating starting and ending values of turbidity before and after the addition of varied doses of either aluminum chlorohydrate (ACH) or GFT 5100 with CA or mixed gas MBs containing 2.5% CO_2.

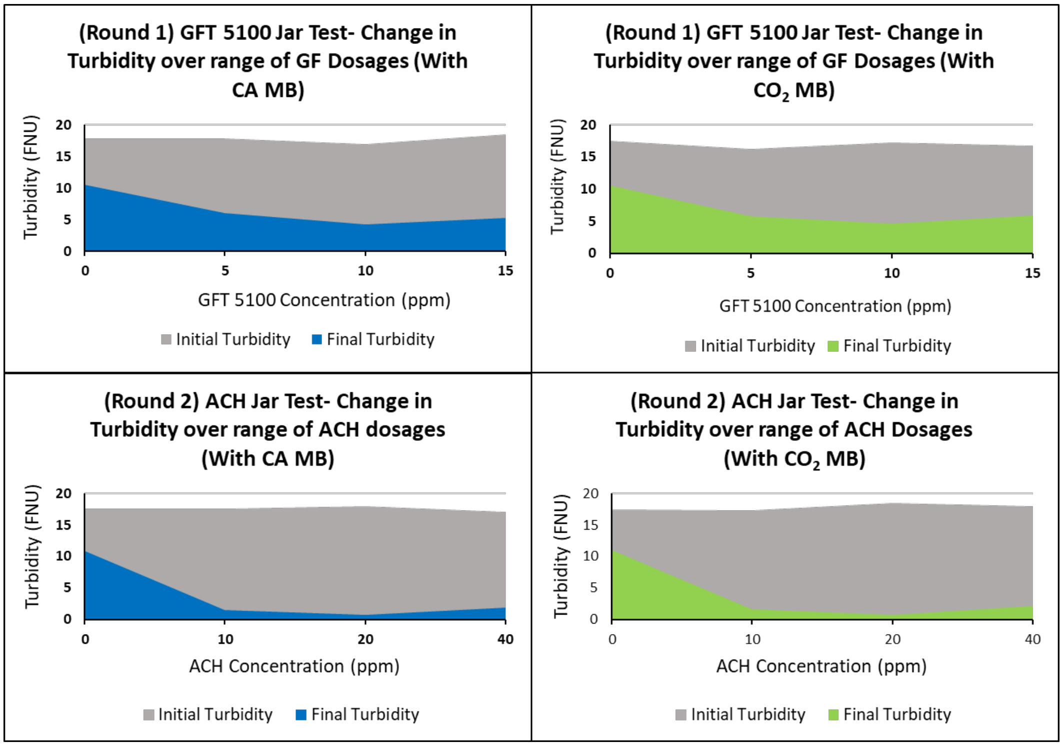


Figure 23. Duplicate results demonstrating change in turbidity before and after the addition of varied doses of GFT 5100 with CA or mixed gas MBs containing 2.5% CO_2.

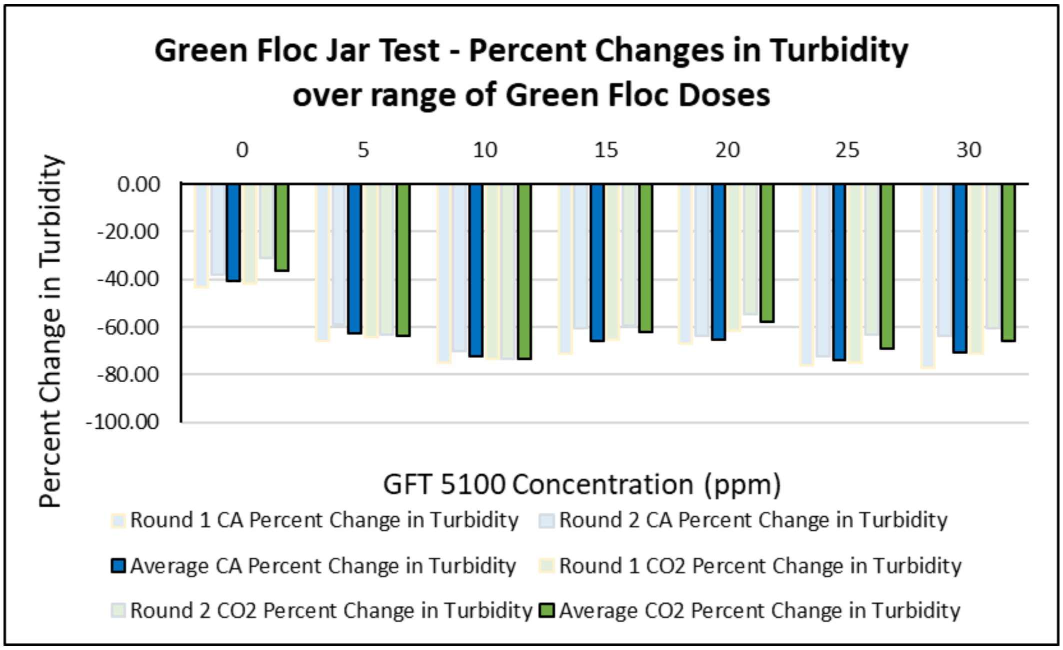
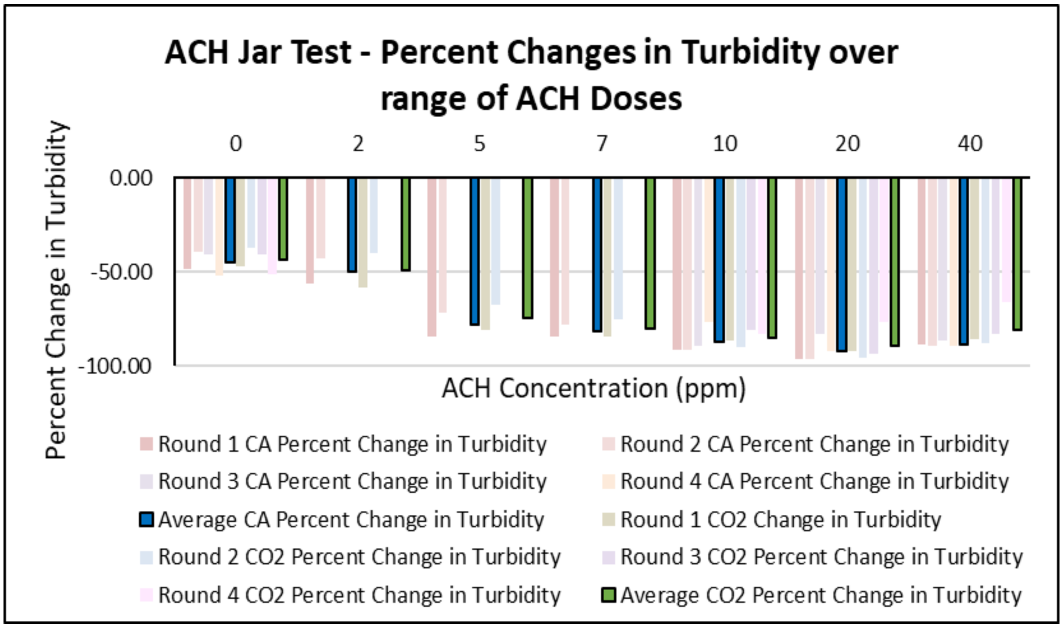


Figure 24. Quadruplicate results demonstrating change in turbidity before and after the addition of varied doses of ACH with CA or mixed gas MBs containing 2.5% CO_2.



3.7 Mixed Gas: MBs + GFT 5100 + ACH

Several dosing combinations of GFT 5100 and ACH were tested to find the optimal doses. The best combinations recorded in the first set of experiments were 5:20 and 10:20 ppm of ACH:GFT 5100, according to Figure 25. Surprisingly, the 100% CA MBs seemed to perform slightly better than the 2.5% CO_2 in most trials.

Another round of experiments was conducted with lower doses (Figure 26), with no significant differences between the 100% CA and 2.5% CO_2 trials. There could be an issue with the order of addition of CO_2 MBs.

Figure 25. Duplicate results demonstrating change in turbidity before and after the addition of varied high doses of ACH combined with GFT 5100 with CA or mixed gas MBs containing 2.5% CO_2.

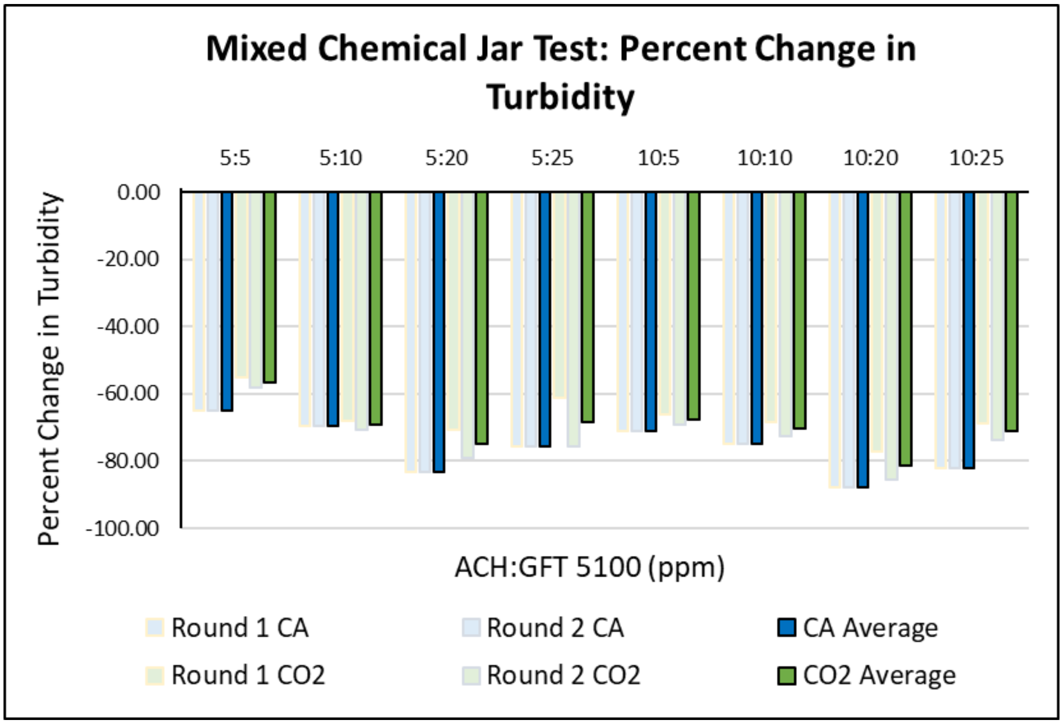
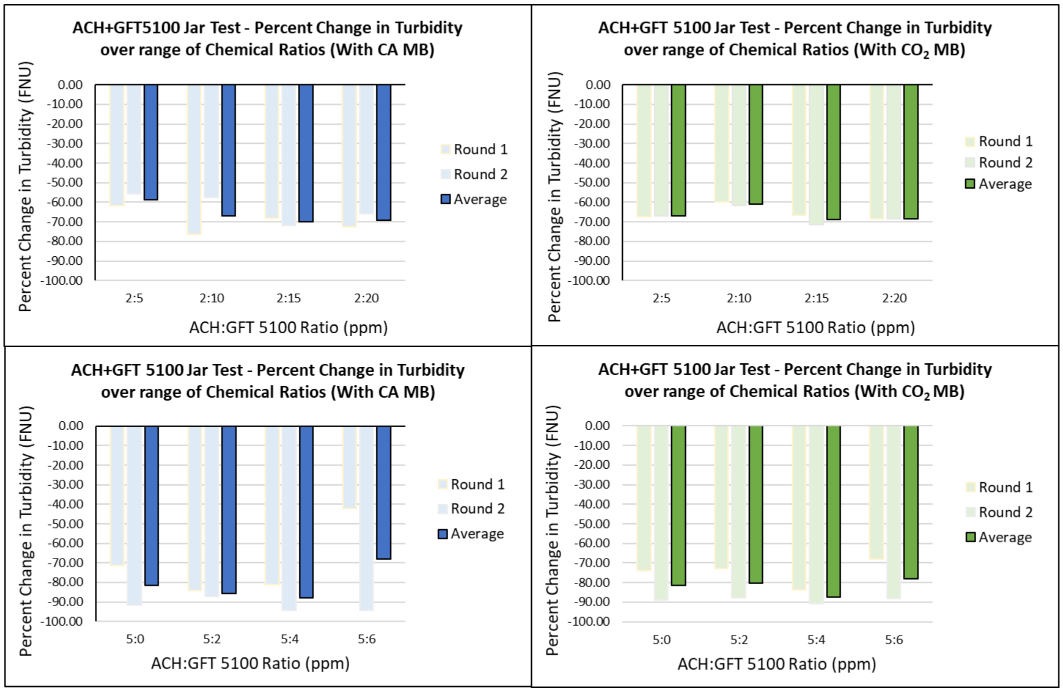


Figure 26. Duplicate results demonstrating change in turbidity before and after the addition of varied low doses of ACH combined with GFT 5100 with CA or mixed gas MBs containing 2.5% CO_2.



3.8 CO_2 Before Chemical Addition

The CO_2 may not have performed better than the CA in the previous experiments, because the CO_2 was added after chemical addition. In the succeeding trials, 50 mL of 5% CO_2 was added before chemical addition to reduce the pH, then 150 mL of 100% CA was added after the mixing stage. The final pH for all the trials were above 6. Switching the order of CO_2 addition seemed to yield better turbidity reductions than the previous experiments, especially with an ACH:GFT 5100 ratio of 5:2 (Figure 27). In that experiment, the average turbidity reduction with CO_2 added was nearly 31% higher than the CA only trial. There may not have been a greater difference between the 5:6 trial (Figure 28), because at that point enough coagulant was added to overcome pH effects. The lower doses of 5:1 and 4:5 (Figure 29) were not enough to trigger charge neutralization and floc formation for algae removal.

Figure 27. Duplicate results demonstrating change in turbidity before and after the addition of varied low doses of ACH (5 or 4 ppm) combined with GFT 5100 (2 or 3 ppm). This is following the procedure where 50 mL of CO_2 is added before chemical addition with 150 mL 100% CA after chemical addition.

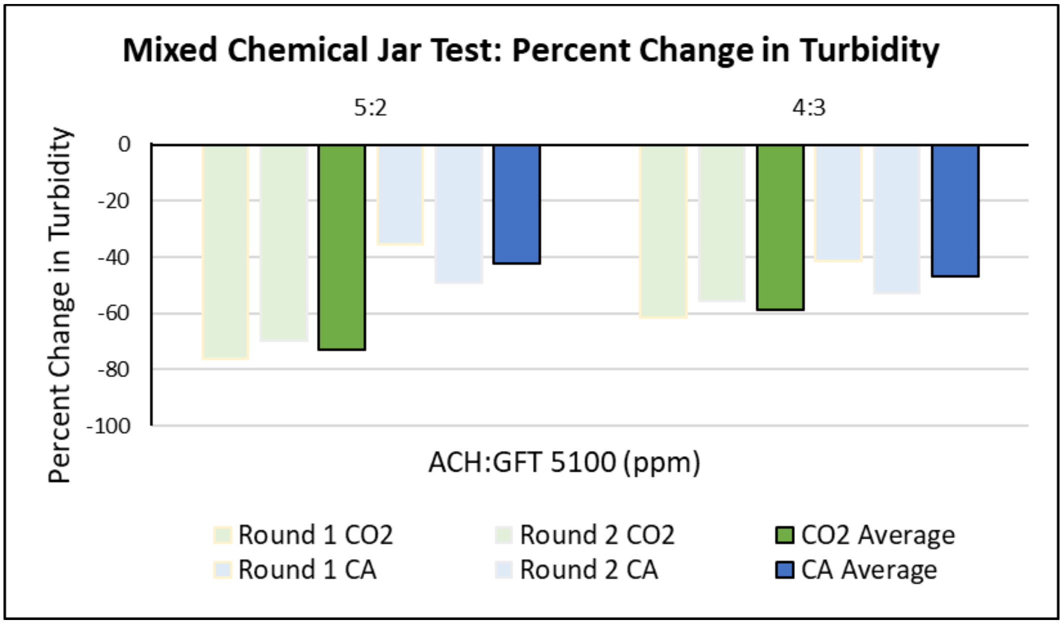


Figure 28. Duplicate results demonstrating change in turbidity before and after the addition of ACH (5 ppm) combined with GFT 5100 (4 or 6 ppm). This is following the procedure where 50 mL of CO_2 is added before chemical addition with 150 mL 100% CA after chemical addition.

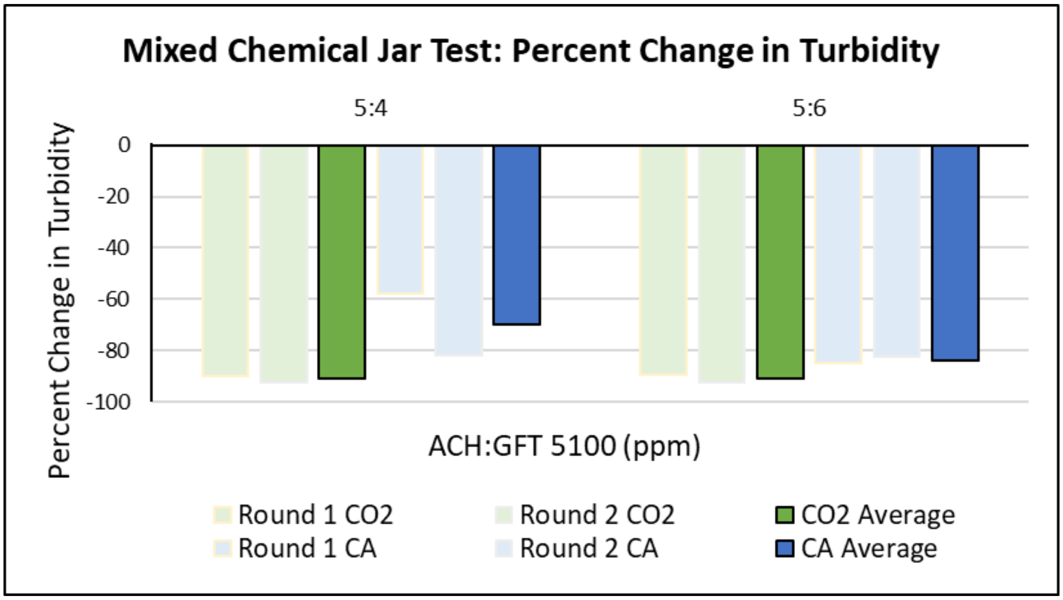
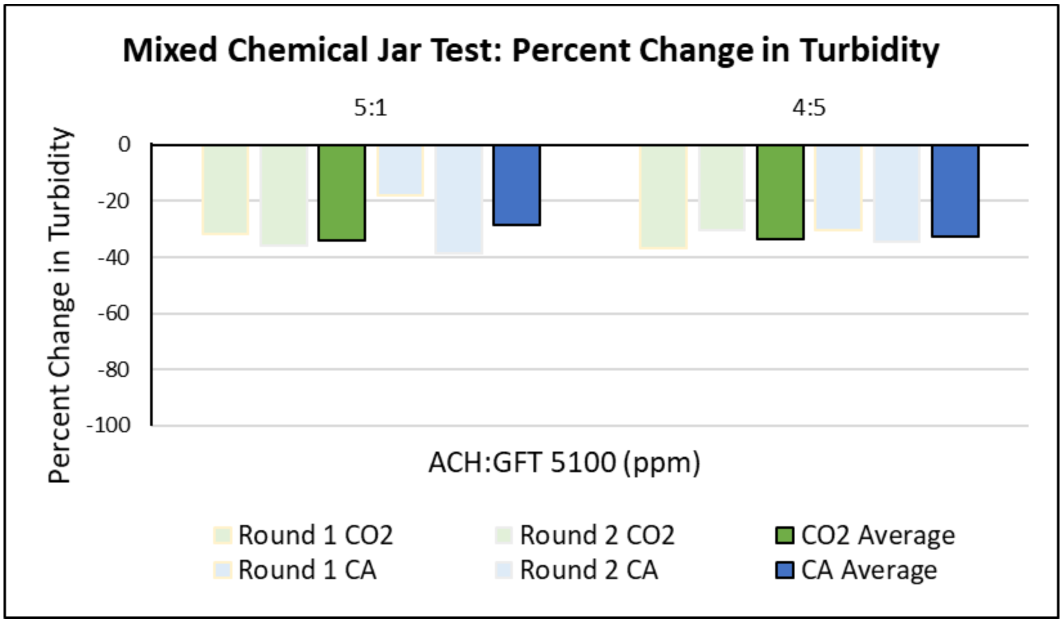


Figure 29. Duplicate results demonstrating change in turbidity before and after the addition of varied low doses of ACH (4 or 5 ppm) combined with GFT 5100 (1 or 5 ppm). This is following the procedure where 50 mL of CO_2 is added before chemical addition with 150 mL 100% CA after chemical addition.



3.9 Algae Density

The algae density tests were conducted using the method where 50 mL of CO_2 was added prior to chemical addition. For both chemical ratios in Figure 30 and Figure 31, there is a clear indication of the positive relationship between percent change in turbidity and a higher initial turbidity. A reason for this may be coagulant overdosage for lower density algal waters, where less positively charged coagulant may be required to neutralize the less abundant negative algal cells. Overdosing with cationic coagulants would result in an overall positive charge of particles instead of neutralizing the particles' charges, causing the algal cells to repel like-positive charges instead of coming together and forming flocs. Furthermore, greater percent turbidity reductions in densely populated waters can be explained by the numerous algal cells having a greater chance to collide with one another during the mixing stage to form larger flocs that can be carried by the MBs.

Figure 30. Turbidity changes over a range of algae densities using a constant dosage of 5 ppm ACH and 4 ppm GFT 5100.

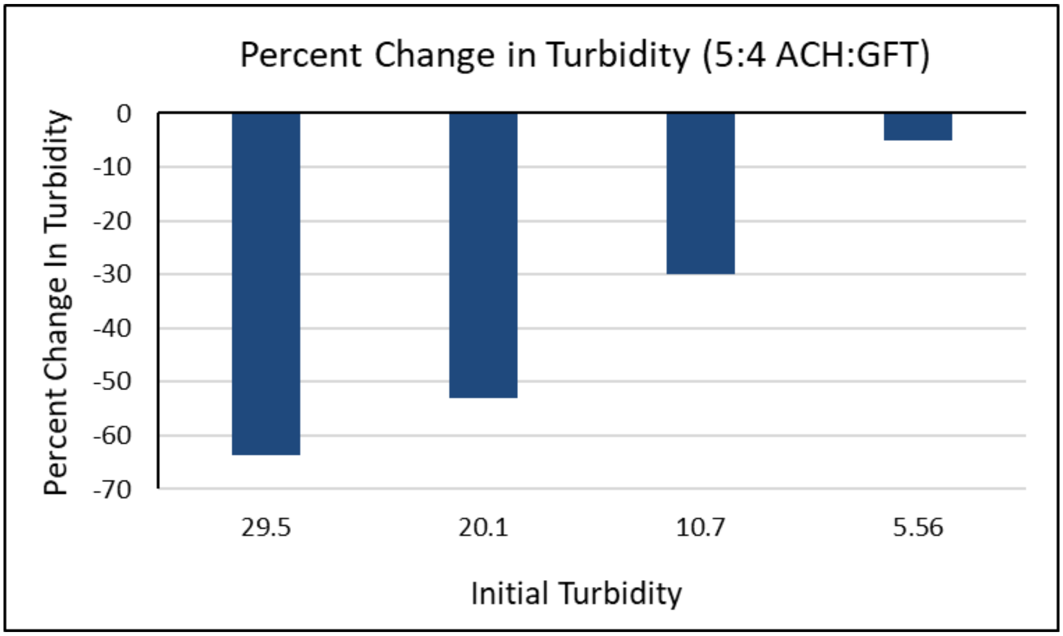
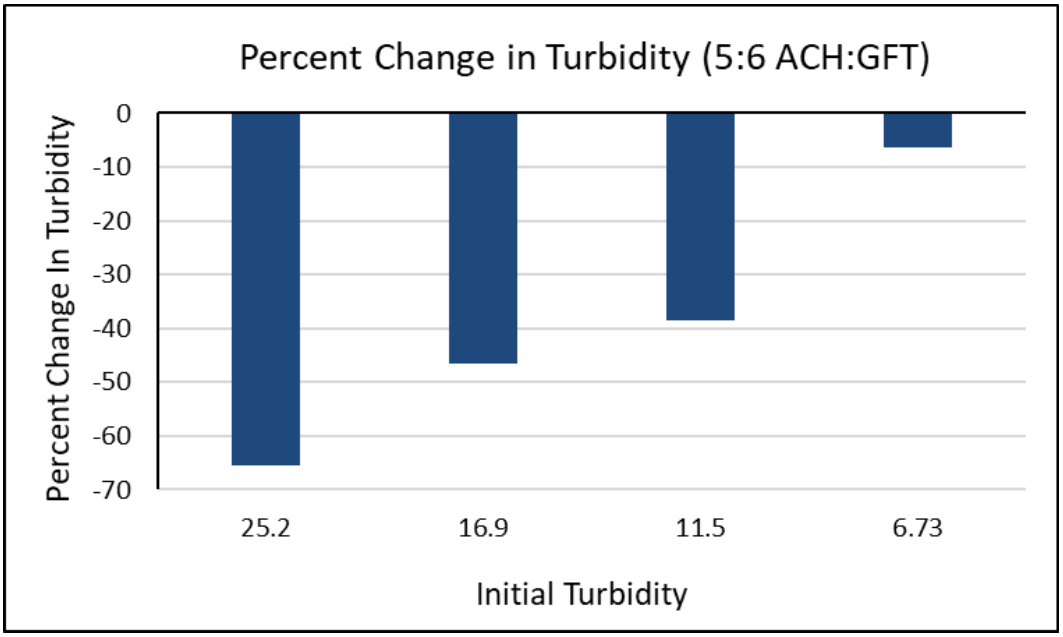


Figure 31. Turbidity changes over a range of algae densities using a constant dosage of 5 ppm ACH and 6 ppm GFT 5100.



3.10 CO_2 Stripping

To ensure environmental safety, the water should be stripped of CO_2 and the pH should return to natural conditions prior to being discharged back into the source. Algal stripping was attempted by adding a second round of 100% CA to the jars after the initial MB step that separates the algae from water. The idea is to force Henry's law, where the solubility of the gas is directly related to the partial pressure of the gas. The partial pressure of CO_2 in ambient air is miniscule, therefore once dissolved CO_2 comes in contact with the air, it will become less soluble and will try to escape the liquid to equilibrate with the atmosphere. In Figure 32 and Figure 33, volumes of the second round of CA bubbles ranged from 0 mL to 800 mL, with algal water of 0 mg/L and 150 mg/L as $CaCO_3$ of added alkalinity, respectively. However, there was no evidence of CO_2 stripping.

This experiment was repeated for 400 mL and 800 mL of CA added into alkalinity-enhanced algal water, and the pH was measured over time up until 240 min after the second microbubble dose was added. Note that to generate the graphs, the initial pH value and middle pH value after initial MBs addition was repeated to visually compare it to the final pH value (Figure 34).

Figure 32. Starting, middle, and ending pH values after adding varying volumes of 2.5% CO_2 MBs in algae water without added alkalinity.

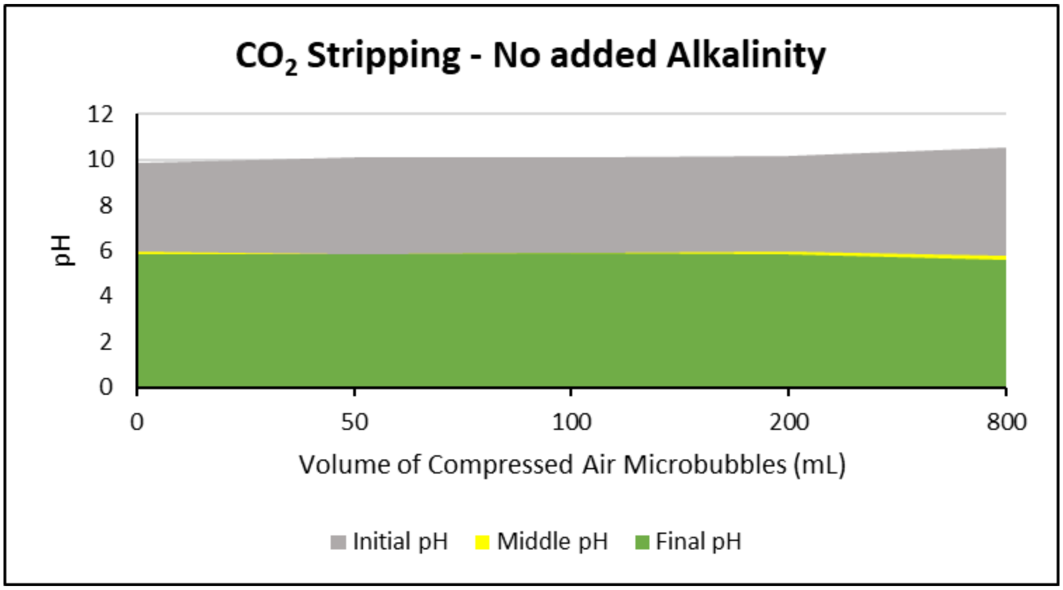


Figure 33. Starting, middle, and ending pH values after adding varying volumes of 2.5% CO_2 MBs in algae water with added alkalinity.

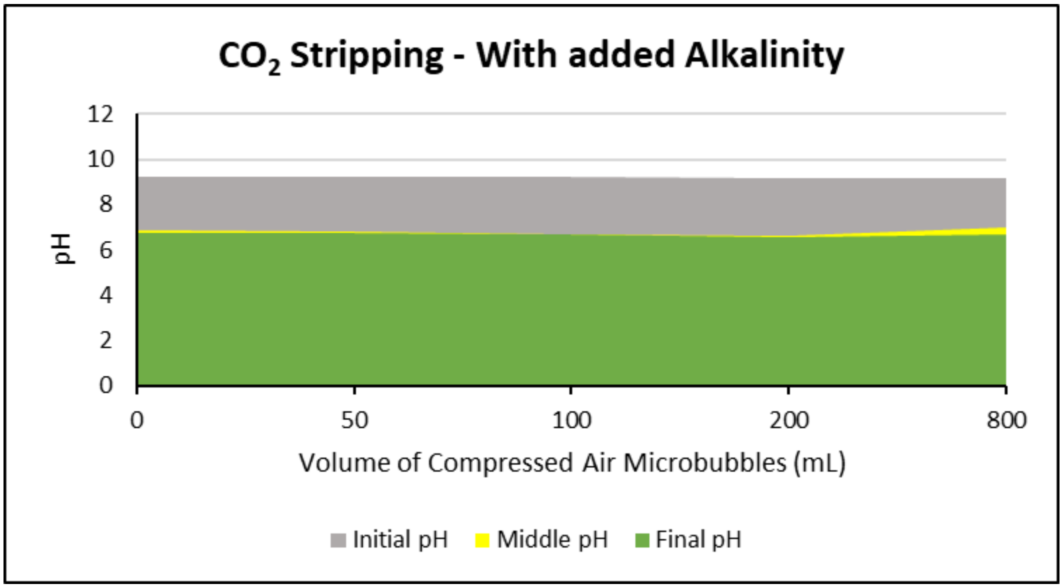
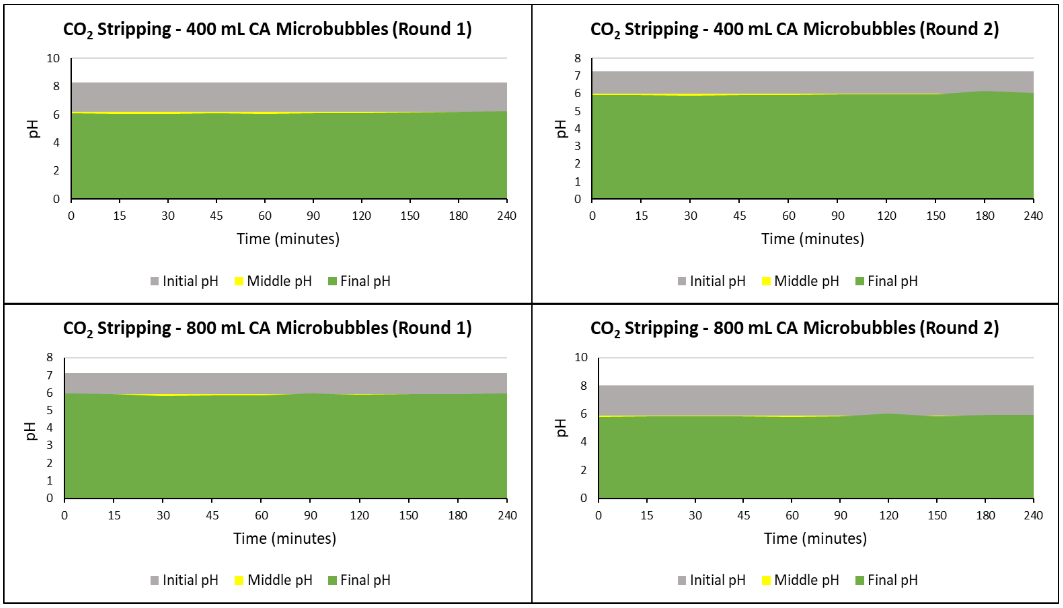


Figure 34. Starting, middle, and ending pH values after adding 400 mL or 800 mL of 2.5% CO_2 MBs over time.



These trials did yield evidence of CO_2 stripping as well. The MBs may not be the correct size for aeration and CO_2 stripping. Larger bubbles generated by fine or coarse bubble diffusers may work better as opposed to MBs infused with DI water, especially paired with baffles or other means to promote mixing and turbulence (Kang et al. 2017). This will provide more volume of air to interact with the CO_2 bubbles in contact with the ambient air to act as a catalyst to Henry's Law.

4 Conclusions and Recommendations

4.1 Conclusions

The following conclusions were drawn from this bench-scale study:

- CO_2 MBs can drastically lower pH, even with small additions, but there are diminishing returns as the CO_2 approaches saturation.
- Additional alkalinity reduces pH from CO_2 MB treatment, and a mixture of CO_2 and CA is required to reach the ideal pH range of 6–7.
- GFT 5100 seems to be most effective between pH 6 and 7.
- We did not observe a beneficial pH effect at the coagulant doses applied when adding the CO_2 after chemical addition. However, when CO_2 was introduced before the chemicals, a beneficial effect was observed. One trial resulted in 31% higher turbidity reductions.
- There seems to be a positive relationship between percent change in turbidity and a higher initial turbidity.
- pH reequilibrium was not achieved using the methods described in this report.

4.2 Recommendations

There is some evidence that indicates that lowering the pH with CO_2 may enhance the DAF coagulation process. More experiments are required to determine the extent of the benefits.

Future bench-scale experiment recommendations include the following:

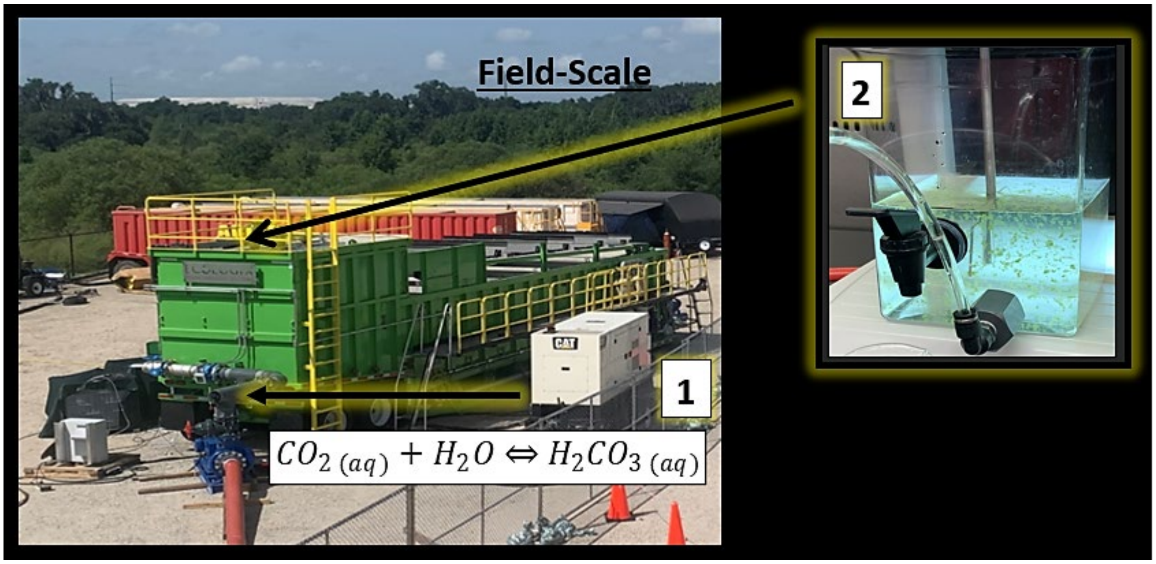
- Measuring chlorophyll and cell density counts in addition to turbidity to have a better proxy for algae removal
- Conducting air stripping experiments with larger bubbles that are not infused with water
- Comparing different doses required to achieve similar turbidity and chlorophyll reductions for trials of 100% CA MBs or 5% CO_2 MBs; This will determine whether a 25% chemical reduction can be achieved by introducing the CO_2 MBs
- Determining effect of algae age and health (% yield) with algae removal performance

Although pH reequilibrium was unsuccessful by injecting a second round of 100% CA MBs, alternative methods such should be explored in the future.

Introducing larger bubbles and turbulence should catalyze Henry's Law. Another option could be adding limestone filters, sodium bicarbonate, or soda ash to increase alkalinity and pH. However, the pH targeted in this study suffices to meet Florida's Class 1 water body pH criteria of 6–8.5 (Unsell 2009), and is near the EPA's suggestion of a minimum of 6.5 in freshwater to sustain aquatic organisms (Suter et al. 2024).

If the coagulation or flocculation benefits hypothesized by the CO_2 addition into the DAF treatment are confirmed, future studies will include assessing the feasibility and scalability of integrating the exhaust from the HABITATS generators (a source for CO_2) into the DAF process. According to Reşitoğlu et al. 2014, diesel exhaust gas composition includes 12% CO_2 (Reşitoğlu et al. 2014). Figure 35 demonstrates the field-scale concept. In the field; however, there may be some trial and error determining the appropriate CO_2 dose to synergize with the natural water's alkalinity to achieve the optimal pH range for coagulation. Also, it would be interesting to sample the effluent water and test the pH after treatment to see if the pH reequilibrated after the water traveled though the lamella tubes and spilled over the weir.

Figure 35. Field-scale concept of CO_2 injection, where CO_2 will be sourced from the generators powering HABITATS and fed into the influent plumbing line prior to coagulant and flocculant addition to enhance the process.



Transforming a waste (generator exhaust) to a resource that has the potential to reduce coagulant demand for DAF without sustained environmental impact would reduce operational costs and environmental risks in HAB mitigation efforts.

Bibliography

Anderson, Donald M., Elizabeth Fensin, Christopher J. Gobler, Alicia E. Hoeglund, Katherine A. Hubbard, David M. Kulis, Jan H. Landsberg, et al. 2021. "Marine Harmful Algal Blooms (HABs) in the United States: History, Current Status and Future Trends." *Harmful Algae* 102 (101975): 1–37. https://doi.org/10.1016/j.hal.2021.101975.

Anderson, Donald M., Porter Hoagland, Yoshi Kaoru, and Alan W White. 2000. *Estimated annual economic impacts from harmful algal blooms (HABs) in the United States*. WHOI-2000-11. Woods Hole, MA: Woods Hole Oceanographic Institution. https://apps.dtic.mil/sti/citations/ADA386861.

Anderson, Donald. 2012. "HABs in a Changing World: a Perspective on Harmful Algal Blooms, their Impacts, and Research and Management in a Dynamic Era of Climactic and Environmental Change." *Harmful Algae* 2012 (2012): 3–17. https://pubmed.ncbi.nlm.nih.gov/26640829.

Bang, Jun-Hwan, Wonbaek Kim, Kyun Sun Song, Chi Wan Jeon, Soo Chun Chae, Hwan-Joo Cho, Young Nam Jang, and So-Jin Park. 2014. "Effect of Experimental Parameters on the Carbonate Mineralization with $CaSO_4{\cdot}2H_2O$ Using CO_2 Microbubbles." *Chemical Engineering Journal* 244: 282–287. https://doi.org/10.1016/j.cej.2014.01.072.

Bechard, Andrew. 2019. "Red Tide at Morning, Tourists Take Warning? County-Level Economic Effects of HABs on Tourism Dependent Sectors." *Harmful Algae* 85: 101689. https://doi.org/10.1016/j.hal.2019.101689.

Berdalet, Elisa, Lora E. Fleming, Richard Gowen, Keith Davidson, Philipp Hess, C. Lorraine Backer, Stephanie K. Moore, Porter Hoagland, and Henrik Enevoldsen. 2015. "Marine Harmful Algal Blooms, Human Health and Wellbeing: Challenges and Opportunities in the 21st Century." *Journal of the Marine Biological Association of the United Kingdom* 96 (1): 61–91. https://doi.org/10.1017/s0025315415001733.

Campobasso, M., M. Ibrahim, A. Chisholm, J. Miazek, M. Page. 2024. "pH-Pivoting for Algae Coagulation." Mendeley Data, V1. https://data.mendeley.com/datasets/dp3zs5s2rn/1.

Diaz, Robert J., and Rutger Rosenberg. 2008. "Spreading Dead Zones and Consequences for Marine Ecosystems." *Science* 321 (5891): 926–929. https://www.science.org/do/10.1126/science.1156401.

Dunnivant, Frank M. 2004. *Environmental Laboratory Exercises for Instrumental Analysis and Environmental Chemistry: Determination of Alkalinity of Natural Waters*. Hoboken, NJ: John Wiley & Sons, Inc. https://onlinelibrary.wiley.com/doi/book/10.1002/0471660280.

Ghernaout, Djamel, Noureddine Elboughdiri, Saad Ghareba, and Alsamani Salih. 2020. "Coagulation Process for Removing Algae and Algal Organic Matter-An Overview." *Open Access Library Journal* 07 (04): 1–21. http://dx.doi.org/10.4236/oalib.1106272.

Kang, J., G. Kwon, J. H. Nam, Y. O. Kim, and D. Jahng. 2017. "Carbon Dioxide Stripping from Anaerobic Digestate of Food Waste Using Two Types of Aerators." *International Journal of Environmental Science and Technology* 14: 1397–1408. https://doi.org/10.1007/s13762-017-1250-1.

Kim, Mi-Sug, and Dong-Heui Kwak. 2014. "Evaluation of Initial Collision-Attachment Efficiency Between Carbon Dioxide Bubbles and Algae Particles for Separation and Harvesting." *Water Science and Technology* 69 (12): 2482–2491. https://doi.org/10.2166/wst.2014.171.

Li, Na, Pengcheng Wang, Shaohua Wang, Chenjie Wang, Hao Zhou, Suman Kapur, Junyan Zhang, and Yongxin Song. 2022. "Electrostatic Charges on Microalgae Surface: Mechanism and Applications." *Journal of Environmental Chemical Engineering* 10 (3). https://doi.org/10.1016/j.jece.2022.107516.

Liu, Shihong, Husam A. Abu Hajar, Guy Riefler, and Ben J. Stuart. 2018. "Investigation of Electrolytic Flocculation for Microalga Scenedesmus Sp. Using Aluminum and Graphite Electrodes." *RSC Advances* 8 (68): 38808–38817. https://doi.org/10.1039%2Fc8ra08101h.

Manuel, John. 2014. "Nutrient Pollution: A Persistent Threat to Waterways." *Environmental Health Perspectives* 122 (11): A304–A309. https://doi.org/10.1289%2Fehp.122-A304.

NOAA. 2023. "The Atmosphere." *JetStream*. Accessed February 01, 2024. https://www.noaa.gov/jetstream/atmosphere.

Orenda Technologies. 2020. "CO2 and pH: Understanding Henry's Law." *Orenda Technologies Blog*, August 24, 2020. https://blog.orendatech.com/co2-and-ph-henrys-law.

Page, Martin, Bruce MacAllister, Marissa Campobasso, Angela Urban, Catherine Thomas, Clinton Cender, Clint Arnett, et al. 2021. *Optimizing the Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS)*. ERDC TR-21-18. Vicksburg, MS: US Army Corps of Engineers Engineer Research and Development Center. http://dx.doi.org/10.21079/11681/42223.

Page, Martin, Bruce MacAllister, Angela Urban, Chris Veinotte, Irene MacAllister, Kaytee Pokrzywinski, Jim Riley, et al. 2020. *Harmful Algal Bloom Interception, Treatment, and Transformation System, "HABITATS": Pilot Research Study Phase I - Summer 2019*. ERDC TR-20-1. Vicksburg, MS: US Army Corps of Engineers Engineer Research and Development Center. http://dx.doi.org/10.21079/11681/35214.

Reşitoğlu, İbrahim Aslan, Kemal Altinişik, and Ali Keskin. 2014. "The Pollutant Emissions from Diesel-Engine Vehicles and Exhaust Aftertreatment Systems." *Clean Technologies and Environmental Policy* 17 (2015): 15–27. https://doi.org/10.1007/s10098-014-0793-9.

Saththasivam, Jayaprakash, Oluwaseun Ogunbiyi, Jenny Lawler, Radee Al-Rewaily, and Zhaoyang Liu. 2022. "Evaluating Dissolved Air Flotation for Oil/Water Separation Using a Hybridized Coagulant of Ferric Chloride and Chitosan." *Journal of Water Process Engineering* 47: 102836. https://doi.org/10.1016/j.jwpe.2022.102836.

Suter, Glenn, Susan Cormier, Kate Schofield, Jaime Gilliam, and Chad Barbour. 2024. "pH." *CADDIS Volume 2: Sources, Stressors and Responses*. Washington, DC: EPA, last updated February 15, 2024. https://www.epa.gov/caddis-vol2/ph.

Takahashi, Masayoshi. 2005. "ζ Potential of Microbubbles in Aqueous Solutions: Electrical Properties of the Gas-Water Interface." *Journal of Physical Chemistry B* 109 (46): 21858–21864. https://doi.org/10.1021/jp0445270.

Unsell, David. 2009. "Appendix 10-1: Lake Okeechobee Operating Permit Annual Report for Water Year 2008." *South Florida Environmental Report: Volume I*. Operating Permit Annual Report for the Florida Department of Environmental Protection. West Palm Beach, FL: South Florida Water Management District. https://apps.sfwmd.gov/sfwmd/SFER/2009_SFER/v1/appendices/v1_app10-1.pdf.

UTEX. n.d. "BG-11 Medium Recipe." UTEX Culture Collection of Algae. Accessed July 2023. https://web.biosci.utexas.edu/utex/Media%20PDF/bg-11-medium.pdf.

Water Science School. 2018. "Alkalinity and Water." USGS, August 07, 2018. Accessed January 29, 2024. https://www.usgs.gov/special-topics/water-science-school/science/alkalinity-and-water.

Wiley, Patrick E., Kristine J. Brenneman, and Arne E. Jacobson. 2009. "Improved Algal Harvesting Using Suspended Air Flotation." *Water Environment Research* 81 (7): 702–708. https://doi.org/10.2175/106143009x407474.

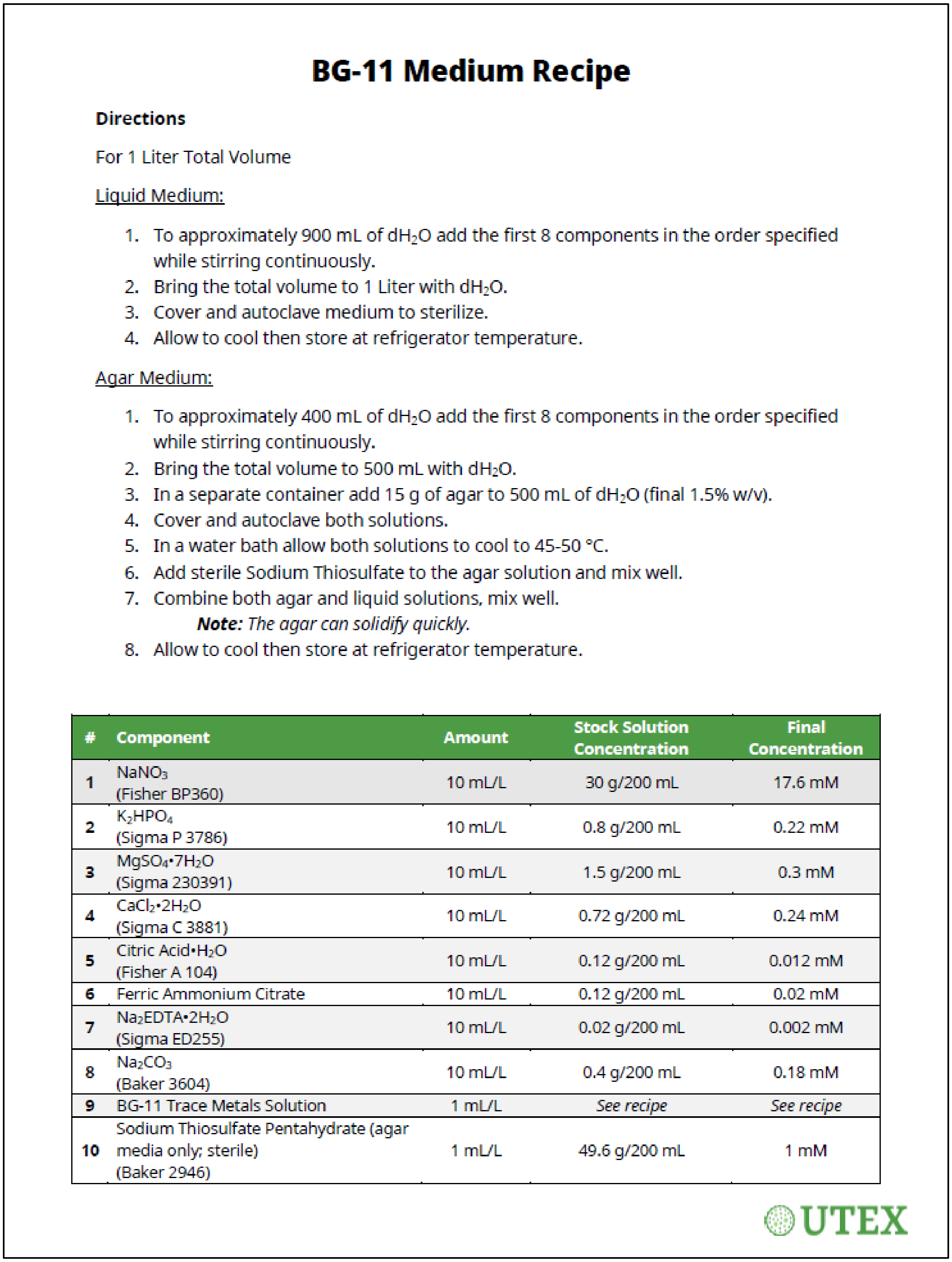
Water Resources Development Act of 2018, Pub. L. No. 115-270, 132 Stat. 3774 § 1109 (2018). https://www.govinfo.gov/content/pkg/PLAW-115publ270/pdf/PLAW-115publ270.pdf.

Xu, Ling, Feng Wang, Hua-Zhong Li, Zan-Min Hu, Chen Guo, and Chun-Zhao Liu. 2010. "Development of an Efficient Electroflocculation Technology Integrated with Dispersed-Air Flotation for Harvesting Microalgae." *Journal of Chemical Technology and Biotechnology* 85 (11): 1504–1507. https://doi.org/10.1002/jctb.2457.

Appendix: BG-11 Growth Medium for Algae Cultivation

Below is the BG-11 growth medium developed by the University of Texas (UTEX) to cultivate algae in the lab (Figure A-1). The recipe includes the components and concentrations of each component for the base medium, as well as components and concentrations for the trace metals solution to be added with the base medium. Each medium is made in a 1 L solution, with 900 mL of volume from the components and the remainder topped off with deionized (DI) water. The base medium must be sterilizer and cooled before usage. Both mediums are recommended to be stored at refrigerator temperature.

Figure A-1. University of Texas (UTEX) BG-11 growth medium recipe. (Image reproduced from UTEX, n.d. Public domain.)



BG-11 Medium Recipe

Directions

For 1 Liter Total Volume

Liquid Medium:

1. To approximately 900 mL of dH_2O add the first 8 components in the order specified while stirring continuously.
2. Bring the total volume to 1 Liter with dH_2O.
3. Cover and autoclave medium to sterilize.
4. Allow to cool then store at refrigerator temperature.

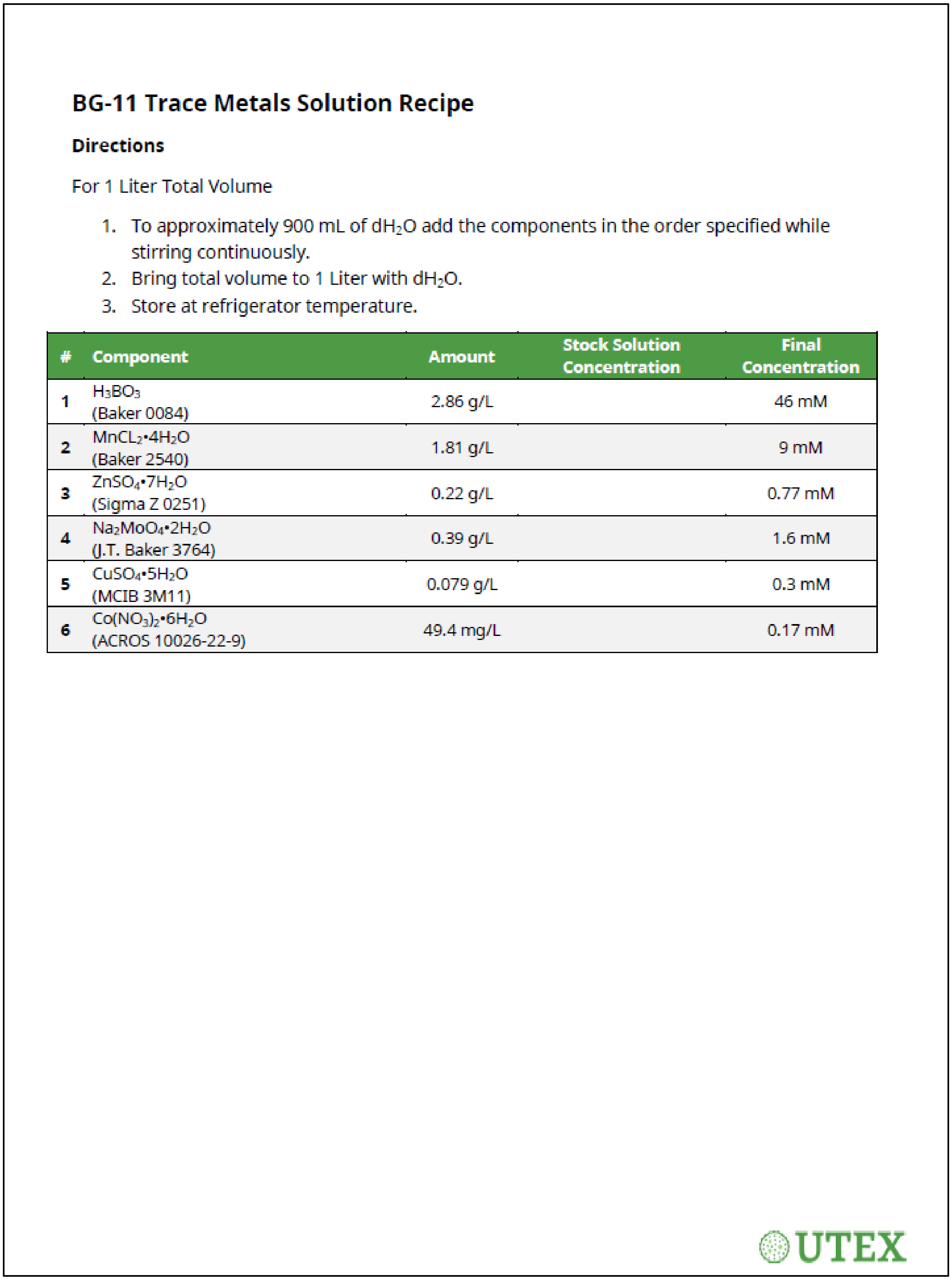
Agar Medium:

1. To approximately 400 mL of dH_2O add the first 8 components in the order specified while stirring continuously.
2. Bring the total volume to 500 mL with dH_2O.
3. In a separate container add 15 g of agar to 500 mL of dH_2O (final 1.5% w/v).
4. Cover and autoclave both solutions.
5. In a water bath allow both solutions to cool to 45-50 °C.
6. Add sterile Sodium Thiosulfate to the agar solution and mix well.
7. Combine both agar and liquid solutions, mix well.
   Note: *The agar can solidify quickly.*
8. Allow to cool then store at refrigerator temperature.

#	Component	Amount	Stock Solution Concentration	Final Concentration
1	$NaNO_3$ (Fisher BP360)	10 mL/L	30 g/200 mL	17.6 mM
2	K_2HPO_4 (Sigma P 3786)	10 mL/L	0.8 g/200 mL	0.22 mM
3	$MgSO_4 \cdot 7H_2O$ (Sigma 230391)	10 mL/L	1.5 g/200 mL	0.3 mM
4	$CaCl_2 \cdot 2H_2O$ (Sigma C 3881)	10 mL/L	0.72 g/200 mL	0.24 mM
5	Citric Acid•H_2O (Fisher A 104)	10 mL/L	0.12 g/200 mL	0.012 mM
6	Ferric Ammonium Citrate	10 mL/L	0.12 g/200 mL	0.02 mM
7	$Na_2EDTA \cdot 2H_2O$ (Sigma ED255)	10 mL/L	0.02 g/200 mL	0.002 mM
8	Na_2CO_3 (Baker 3604)	10 mL/L	0.4 g/200 mL	0.18 mM
9	BG-11 Trace Metals Solution	1 mL/L	*See recipe*	*See recipe*
10	Sodium Thiosulfate Pentahydrate (agar media only; sterile) (Baker 2946)	1 mL/L	49.6 g/200 mL	1 mM

UTEX

Figure A-1 (cont.). University of Texas (UTEX) BG-11 growth medium recipe.



BG-11 Trace Metals Solution Recipe

Directions

For 1 Liter Total Volume

1. To approximately 900 mL of dH_2O add the components in the order specified while stirring continuously.
2. Bring total volume to 1 Liter with dH_2O.
3. Store at refrigerator temperature.

#	Component	Amount	Stock Solution Concentration	Final Concentration
1	H_3BO_3 (Baker 0084)	2.86 g/L		46 mM
2	$MnCL_2$•$4H_2O$ (Baker 2540)	1.81 g/L		9 mM
3	$ZnSO_4$•$7H_2O$ (Sigma Z 0251)	0.22 g/L		0.77 mM
4	Na_2MoO_4•$2H_2O$ (J.T. Baker 3764)	0.39 g/L		1.6 mM
5	$CuSO_4$•$5H_2O$ (MCIB 3M11)	0.079 g/L		0.3 mM
6	$Co(NO_3)_2$•$6H_2O$ (ACROS 10026-22-9)	49.4 mg/L		0.17 mM

Abbreviations

ACH	Aluminum chlorohydrate
CA	Compressed air
CERL	Construction Engineering Research Laboratory
DAF	Dissolved air flotation
DI	Deionized
EL	Environmental Laboratory
ERDC	Engineer Research and Development Center
FNU	Formazin Nephelometric Units
GFT 5100	Greenfloc 5100
HAB	Harmful algal bloom
HABITATS	Harmful Algal Bloom Interception, Treatment, and Transformation System
MB	Microbubbles
PNNL	Pacific Northwest National Laboratory
USACE	US Army Corps of Engineers
UTEX	University of Texas
WRDA	Water Resources Development Act

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14. ABSTRACT

Harmful algal blooms (HABs) threaten recreational waters and public supplies across the US, causing detrimental economic and environmental effects to communities. HABs can be mitigated with dissolved air flotation (DAF) treatment, which requires addition of pH-sensitive charged chemicals to neutralize algae, allowing them to attach to microbubbles and float to the surface. During HAB events and photosynthesis, algae raise the pH to levels that are not ideal for DAF. Traditionally, pH is reduced with a strong acid; however, this adds operational cost and permanently adjusts the water's pH. This study assessed an approach that might allow for infusing CO_2 from diesel-powered electricity generators into the water prior to DAF treatment. It was hypothesized that formation of carbonic acid could temporarily reduce the pH. Results showed that 2.5%–5.0% CO_2 mixed within compressed air can achieve pH levels between 6–7 in algal water with an initial pH of 9–11 and alkalinity of 150 mg/L as $CaCO_3$. Further, dosing CO_2 before chemical addition yielded a 31% improvement in water clarification. Returning the pH back to natural levels was not achieved using ambient air microbubbles; however, coarse bubble air spargers should be tested to provide more volumetric capacity for CO_2 absorption.

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Algal blooms–Management; Algae; Carbon dioxide; Coagulation; Dissolved air flotation; Hydrogen-ion concentration; Jar test; pH; Water quality

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