

# Efficacy of Algaecides and Novel Ozone Nanobubble Technology on Prevention and Management of HABs

## USACE Harmful Algal Bloom Research & Development Initiative



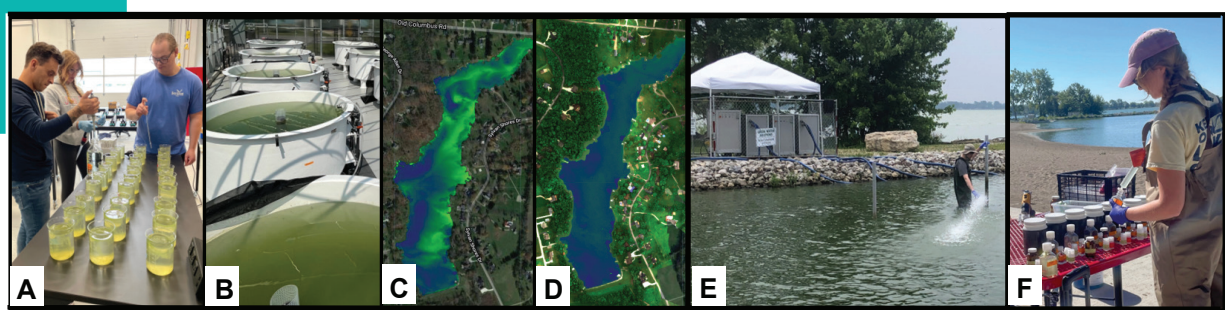
Delivering scalable freshwater HAB prevention, detection, and management technologies through collaboration, partnership, and cutting-edge science.

Lead: Heather Raymond, The Ohio State University

### Problem

Lab and field trials have demonstrated the efficacy of algaecides on cyanobacteria control at warmer temperatures, but data on treatment potential at lower temperatures is limited. There are increasing reports of cyanotoxin producing harmful algal blooms (HABs) in temperate regions under cooler conditions. Faced with limited options, water managers may apply algaecides that could have little to no benefit, but high cost. Having a better understanding of temperature limitations for different algaecide formulations could provide a cost savings and increase effectiveness.

Nanobubble ozone treatment (NBOT) is an emerging alternative HAB prevention and control strategy with potential effectiveness at lower temperatures. By incorporating ozone into nanobubbles, ozone may persist for longer periods, diffuse slower, increase hydroxyl radical production, and increase reaction times with contaminants. Preliminary studies in Florida and Ohio have yielded promising results, but the modes of action for cyanobacteria control have not been fully elucidated and it is unclear how changing environmental conditions impact treatment and dose requirements. How this treatment potentially impacts nutrient cycling is also poorly understood. Controlled studies are limited and full-scale sustained lake treatments have not been conducted. A lack of data on potential impacts to nontarget organisms has created barriers for approval of larger scale treatment trials.



**Figure 1.** Example lab, mesocosm, and full scale treatment trials: (A) algaecide beaker experiments; (B) mesocosm NBOT and algaecide comparison; (C) NBOT lake treatment trial, pretreatment; (D) NBOT late treatment trial, posttreatment; and (E and F) NBOT state park beach treatment trial.

### Objective

This project aims to evaluate effectiveness and potential impact to nontarget organisms of NBOT technology for cyanobacteria control and nutrient abatement. NBOT treatments are also being compared to traditional registered algaecides (multiple copper and hydrogen peroxide based formulations) and efficacy of both treatments at lower temperatures and on cold-tolerant cyanobacteria is being evaluated. Experiments have been conducted in the lab, in controlled mesocosms, and in full-scale field trials. Overall, this project will provide scientifically defensible data that water managers need to make informed decisions related to algaecide use and alternative NBOT treatments.

### Approach

**NBOT Lab Experiments.** Controlled experiments aimed to quantify bubble size distribution, density, lifetime, and zeta potential, and the aqueous ozone and hydroxyl radical produced in solution during and following NBOT treatment. Production of high densities of nanobubbles was confirmed using a nanosight, but microbubbles were also produced in the bench scale unit. The total hydroxyl radical production from nanobubble collapse alone (no ozone addition) was found to be minimal (less than 5  $\mu\text{g/L}$  over 100 days) and insufficient for the oxidation demand for most treatment needs. These results indicate that nanobubble technology without ozone gas claiming to work through the action of hydroxyl radical production is not a suitable treatment method. This finding is important, since several companies currently market nanobubble-only treatment technologies. In NBOTs, the majority of ozone is released to aqueous phase within the unit, less than 10% persists within nanobubbles, and a small fraction is converted to hydroxyl radical. Year 3 NBOT lab experiments will aim to quantify hydrogen peroxide production, investigate effects of NBOT treatment on nutrient cycling and dissolved organic material (DOM), and evaluate ozone dosing requirements based on variable water quality parameters.

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### Approach (cont.)

**Algaecide Beaker Experiments.** Low-temperature (10°C, 15°C, and 20°C) replicated algaecide experiments using 5–6 copper and peroxide-based algaecides at three doses were conducted on a spring and fall Grand Lake Saint Marys–sourced *Planktothrix*-dominant bloom and on a higher-temperature (17°C, 22°C, and 27°C) late-summer Lake Erie–sourced *Microcystis* and *Dolichospermum* bloom. The algaecides did not perform well in terms of cyanobacteria reduction in cooler temperatures, yet intercellular toxins were released, which could have implications for drinking water supplies. There were differences in algaecide response between trials, with reduced effectiveness in the spring versus fall collected *Planktothrix* bloom. The warmer Lake Erie–sourced bloom responded best to treatment. Metatranscriptomic analysis is in process.

**Mesocosm Trials.** A mesocosm trial was conducted at Stone Laboratory using Lake Erie–sourced water. Copper and hydrogen peroxide based algaecides were compared to two NBOT ozone doses in a replicated study. The algaecides, applied following recommended label doses, had severe detrimental effects on the zooplankton community while the lower dose NBOT treatment had a positive impact on zooplankton community (increased abundance) and the higher dose NBOT treatment only impacted *Bosmina* populations. Overall, the NBOT treatments had less negative impact to nontarget organisms as compared to algaecides. A second mesocosm trial focused on impact of DOM on NBOT dosing requirements will occur in 2023. Cell staining and metatranscriptomic analyses are being employed to better elucidate mode of action for cyanobacteria control.

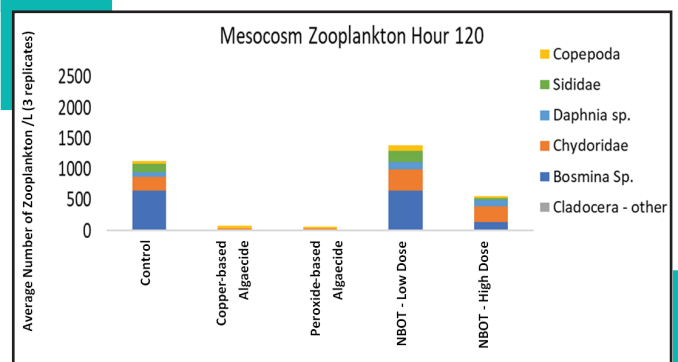


Figure 2. Graph of results.

**Full-Scale NBOT Trials.** Multimonth NBOT trials were conducted at Lake Sylvan and Grand Lake Saint Marys West Beach, and a shorter term stream trial took place at the Saint Marys River. At Lake Sylvan following increased NBOT dose, cyanobacteria concentrations decreased, the community shifted, and recreational advisories were avoided. At a neighboring no-treatment lake with similar bloom, cyanobacteria concentrations increased during the same period and advisories were necessary. Cyanobacteria and toxin concentrations were higher during the Grand Lake Saint Marys beach NBOT trial and treatment effects were localized. Recreational advisories at the treatment beach were reduced compared to neighboring beaches. Repeat beach treatment trials are planned for summer 2023 and additional sampling will occur to better delineate treatment effect and spatial extent from treatment units. A short-term stream trial was conducted in November 2022, and declines in cyanobacteria and toxin concentrations were observed post treatment. An additional stream trial is planned for 2023. How changes in DOM resulting from NBOT treatment affect the phytoplankton community is also being evaluated.

### Partnership/Leveraging Opportunities

The Ohio State University: Eugene Braig, Dr. Justin Chaffin, Dr. Rachel Gabor, Dr. Linda Weavers, Dr. Chris Strasbaugh, Dr. Sami Khanal, Dr. Billy Fagan, Dr. Sam Miller, Haley Kuhn, Josh Fuchs, Jack Deptola, Elyse Bonner, Shannon Thayer, Vinny Anderson, Mark Tischer, Haleigh Fernandez, Autumn Taylor, Keara Stanislawczyk, Ian Crumrine, Holly Stanley, Katie Gaffney, Anne Gerhart, Megan Greige, Matt Romanko, Neha Joshi, and Mark Bola. University of Florida: Dr. H. Dail Laughinghouse III, Dr. David Berthold, Dr. Forrest Lefler, Maximiliano Barbosa, and Jing Hu.

Additional Collaborators: Dr. Peter Moeller (NOAA), Dr. Mike Elovitz (USEPA), Dr. Heath Mash (USEPA), Dr. Stephen Jacquemin (Wright State University), Ohio Department of Natural Resources, Ohio EPA, Sylvan Lake Association, Grand Lake Saint Marys Restoration Commission, and Green Water Solutions LLC.



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