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Ineffectiveness of phosphorus binding treatments in a semi-enclosed area of a large, shallow, and hypereutrophic lake

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Research Article

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Abstract

Hypereutrophic Grand Lake St Marys (GLSM) is a large (52 km^2), shallow (mean depth ~ 1.5 m) reservoir in an agricultural watershed of western Ohio (USA). GLSM suffers from extensive cyanobacterial harmful algal blooms (cHABs) that persist much of the year, resulting in total microcystin concentrations that are often above safe contact levels. Over two summers (2020 and 2021), two phosphorus (P) binding agents (alum and lanthanum/bentonite clay Phoslock, respectively), in conjunction with a P-binding algaecide (SeClear) in 2021, were applied to a 3.24-ha enclosure to mitigate cHAB activity and create a 'safe' recreational space for the public. We evaluated these applications by comparing total phosphorus (TP), total microcystin, total chlorophyll, and phycocyanin concentrations within the enclosure and the adjacent lake. Some evidence for short-term reductions in TP, microcystin, chlorophyll, and phycocyanin concentrations were observed following each P binding treatment, but all parameters rapidly returned to or exceeded pre-application levels within 2–3 weeks after treatment. These results suggest that in-lake chemical treatments to mitigate cHABs are unlikely to provide long-lasting benefits in these semi-enclosed areas of large, shallow, hypereutrophic systems, and resources may be better applied toward reducing external nutrient loads (P and nitrogen) from the watershed.

Impact statement

Hypereutrophic aquatic systems suffering from harmful cyanobacterial blooms have become more common globally in recent decades. These issues have deteriorated drinking water quality, diminished usage and value of recreational and commercial resources, and altered ecosystems (e.g., hypoxic zones and cyanobacterial toxin production). As a result, resource managers have implemented nutrient reduction practices and more focused water treatment technologies. Phosphorus (P) binding agents are often added to hypereutrophic systems to sequester excess P in sediments, theoretically preventing this P from contributing to algal bloom proliferation. This study assessed the efficacy of two common P-binding technologies in a small, semi-enclosed area of a large, shallow, and hypereutrophic lake in an agricultural watershed. Results showed limited evidence of short-term (days to a few weeks) reductions in algal biomass, with no long-lasting (months) benefits associated with these expensive treatments. Water quality improvement efforts are thus better focused on sustainable, watershed-scale nutrient reduction practices.

Introduction

Eutrophication is caused by excess nutrients (P and N) and is one of the most prevalent and concerning water quality issues globally. Excess nutrients are a catalyst for algal blooms (e.g., cyanobacterial harmful algal blooms, cHABs), which alter ecosystem function, reduce ecosystem services and overall water quality, increase algal toxin production, and are accompanied by costs of ~US$2.2–4.6 billion annually for U.S. freshwaters (Treuer et al., 2021). One such system, Grand Lake St Marys (GLSM; Ohio, USA), suffers from frequent cHABs, while also acting as a drinking water resource for the city of Celina (population ~ 10,800) and a recreational resource previously valued at up to US$150 million per year (Davenport and Drake, 2011; Steffen et al., 2014). This relatively large, shallow lake, with an agricultural watershed and cHABs, is typical of many freshwater systems globally.

In shallow systems, the exchange of nutrients between sediments and overlying water (benthic-pelagic coupling) is important for understanding eutrophication and developing management strategies (Griffiths et al., 2017). Inorganic P and N are assimilated into biomass, some of which is transported to and remineralized within or near the sediment–water interface (Baustian et al., 2014), although some remineralization also occurs in the water column (McCarthy et al., 2013). The remaining biomass can be sequestered in sediments, contributing to legacy N and P reservoirs, which can be released later as less labile organic matter is gradually remineralized (e.g., Klump et al. 2020). In addition, phosphate (PO_4^{3-}) adsorbs to sinking sediment particles (i.e., complex with iron or aluminum) under oxic conditions, further contributing to legacy P accumulation within sediments. These complexes prevent P release under oxic conditions, while anoxia facilitates P efflux from sediments (Baustian et al., 2014).

Lake management efforts often use chemical additions that adsorb P as short–term solutions to mitigate cHABs. Practical, political, and economic limitations often hinder the implementation of long-term, sustainable methods for reducing external nutrient inputs (e.g., restoring natural wetlands, agricultural best management practices, etc.; Jančula and MarŠálek, 2011; Nogaro et al., 2013). P-binding chemical treatments, such as aluminum sulfate (alum) or lanthanum bentonite clays (e.g., Phoslock), are somewhat affordable and bind dissolved P, forming floccules that sink to sediments (Epe et al., 2017; Jančula and MarŠálek, 2011; Nogaro et al., 2013). These floccules provide a temporary "cap" on sediments to prevent P release from underlying strata (Jančula and MarŠálek, 2011; Nogaro et al., 2013). The effectiveness and longevity of this sediment cap vary from less than a year to decades, depending on initial treatment dosage, lake morphology (i.e., depth, surface area, stratification, etc.), degree of eutrophication, benthic oxygenation, and biota (e.g., benthic feeding fish, such as carp *Cyprinus carpio*, can disturb sediments (Huser et al., 2016; Nogaro et al., 2013; Zeller and Alperin, 2021)). Meta-analyses on short-term impacts of alum addition in lakes indicate that decreases in total P (65%), chlorophyll (62%), and turbidity (33%) can be expected, but longer-term impacts are highly variable (Huser et al., 2016). Meta-analyses of lanthanum-based clay treatments are not as readily available, likely in part due to the shorter length of time that these products have been to market compared with alum. However, for lanthanum-based clay treatments, several short-term studies reported decreased total P, chlorophyll, and turbidity at similar levels as with alum (Su et al., 2021). Ultimately, these chemical treatments often represent short-term, unsustainable efforts that require repeated applications.

The objective of this study was to evaluate the effects of alum and lanthanum clay treatments on nutrient and chlorophyll dynamics and observe whether the treatments mitigated cHAB biomass and toxicity within a small (3.24 ha) swimming enclosure in GLSM. We expected that the alum application (Summer 2020) would not be successful, since much of the P was already incorporated into algal biomass at the time of application. We hypothesized that applications of a copper-based algaecide/P-binding treatment followed by lanthanum clay (Summer 2021), would more effectively reduce algal biomass (as chlorophyll and phycocyanin) and microcystin concentrations in the enclosure compared to untreated locations in the main lake, since this approach should have broken down algal cells prior to binding P. Results from this study will be useful for resource managers as they balance the often-conflicting objectives of sustainably mitigating eutrophication and cHABs versus an overarching political and societal desire for rapid, tangible improvements in water quality and resource value.

Methods

Study site description

Throughout the last decade (2010–2020), GLSM has experienced recurring cHABs, resulting in overall reductions in lake water quality and recreational value (Jacquemin et al., 2023; Steffen et al., 2014; Wolf and Klaiber, 2017). These blooms are prevalent due to high external nutrient loads from a watershed dominated by agricultural row–crops and livestock production (Hoorman et al., 2008; Jacquemin et al., 2018; OEPA, 2007). GLSM is the largest (52 km^2) inland lake in Ohio, USA; however, with a shallow average depth (~1.5 m), internal loading from legacy nutrients (both N and P) accumulated in sediments can intensify and prolong eutrophication (Jacquemin et al., 2023). These cHABs can persist year-round, including in winter (e.g., winter 2019–2020; Jacquemin et al., 2023), and are dominated by *Planktothrix*, a non-N_2-fixing, filamentous cyanobacterium known to produce N-rich microcystins (Steffen et al., 2014). During peak cHABs, other cyanobacterial taxa (e.g., *Microcystis* and *Aphanizomenon* spp.), are also present, often coinciding with the highest microcystin measurements (Steffen et al., 2014). Historically, total microcystin levels for GLSM were in the 99th percentile for the USA, leading to annual "no contact" warnings and a "distressed" watershed designation, but concentrations have decreased in recent years due to watershed conservation and management practices (Jacquemin et al., 2018). However, microcystin concentrations in most years are still at or above the World Health Organization (WHO) no-contact limit of 24 μg L^{-1} during much of the year (Jacquemin et al., 2023; Steffen et al., 2012; U.S. Environmental Protection Agency, 2009).

Sampling sites

Water samples from two locations in GLSM (Figure 1) were collected from April 2020 through September 2021. Sampling sites were in the northeastern portion of GLSM, one within the West Beach swimming enclosure, where P binding treatments were applied, and one located just outside the enclosure in the main lake. The sites were similar in depth (~ 1 m) and bottom composition (silt/clay with some sand). The West Beach Enclosure is ~3.24 ha (0.0325 km^2), with an average sampled depth of 0.93 m, and a maximum sampled depth of 1.51 m (volume ~ 30,225 m^3). Alterations were made by the Ohio Department of Natural Resources (ODNR) in previous years to reduce water exchange between the main lake and West Beach Enclosure in an effort to promote public recreation. In addition to extending the rock berm, fabric small-mesh and air bubble curtains were installed across the exchange opening between the enclosure and the lake, and ~ 20 aerators were placed throughout the enclosure. Approximately half of the enclosure area was dredged to remove nutrient-rich sediment and replaced with a new sand base immediately prior to the start of this project.

P-binding treatments

GLSM has received several alum treatments in recent years, including numerous pilot projects in smaller areas and multiple large-scale applications. Smaller pilot projects in bays/channels during September 2010 and April 2011 dosed alum/sodium aluminate at rates ranging from 31.6 to 112 mg L^{-1} (Nogaro et al., 2013; Tetra Tech, 2011). Large-scale applications (~30–40% of the entire lake area), costing USD$3–5 million, were conducted by the State of

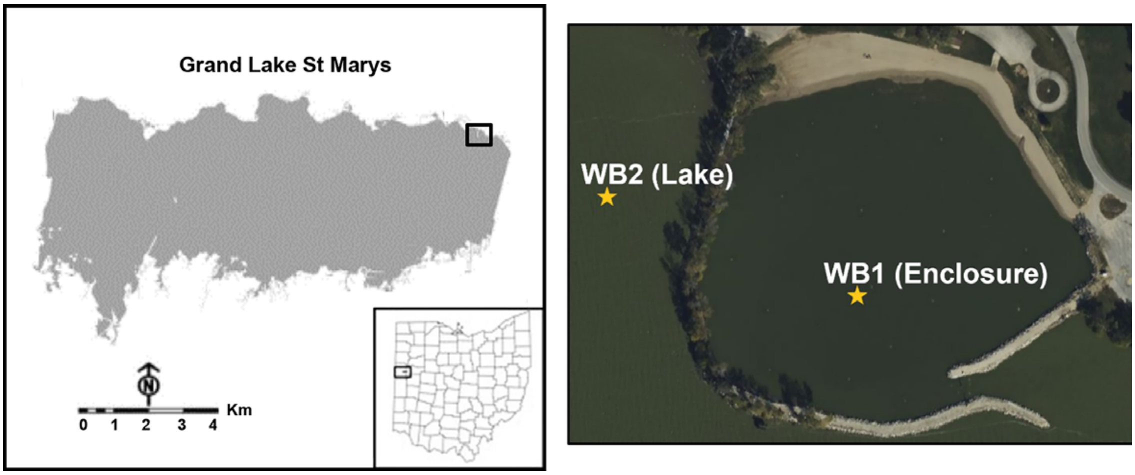

Figure 1. Map of Grand Lake St. Marys showing the location of the West Beach Enclosure (black square) and location in Ohio, USA (modified from Steffen et al., 2014). The site is known locally as 'Dog Tale Lake' or 'Sunset Beach'. Sampling site locations within and outside the enclosure (generated using Google Earth Pro v7.3.4).

Ohio, in collaboration with consulting companies, in June 2011 and April 2012 at dosage rates of 21.5 and 23.6 mg L^{-1}, respectively (Welch et al., 2017). Past alum treatments in GLSM resulted in immediate and appreciable decreases of reactive P, TP, suspended solids, and chlorophyll, but these improvements typically lasted less than a month (OEPA Alum Testing Demo 2011 Lab Data; Nogaro et al., 2013; Welch et al., 2017). Even under ideal conditions, P-binding alum applications in GLSM are predicted (using a combination of depth and area through the Osgood Index) to sustain TP reductions for less than 4.6 years (Huser et al., 2016). Lanthanum clays, such as Phoslock, have not been applied previously in GLSM, but results similar to those from alum applications are expected (Epe et al., 2017).

For this study, the initial alum treatment (granular and premixed with lake water immediately prior to surface application) was conducted on June 9, 2020, and 2,358.7 kg (~80 mg L^{-1}) was applied to the West Beach Enclosure. This dosage rate was consistent with past applications in GLSM. In 2021, a combination of lanthanum-dosed bentonite clay (Phoslock; granular and spread in raw form without premixing) and copper sulfate algacide (SeClear) were applied every 3–4 weeks from May to August 2021 (Table 1). SeClear was applied at 3.75 mg L^{-1} (113.4 kg), and Phoslock was applied at 15 mg L^{-1} (453.6 kg), except for June 11 (748.4 kg; 25 mg L^{-1}).

Sample collection and water quality analyses

Site visits within and outside the West Beach Enclosure (Figure 1) were conducted weekly from April 2020 through September 2021. Physicochemical parameters (e.g., temperature, dissolved oxygen, pH, and conductivity), chlorophyll, phycocyanin, total P (TP), and total microcystins were assessed weekly from April through September to encompass the 'recreation season'. Phosphate (ortho-P) and dissolved aluminum concentrations were measured monthly. A Eureka Manta 2 sonde was used to measure temperature, depth, dissolved oxygen (DO) concentration, pH, and specific conductance. A BBE Moldaenke Algae Torch was used to measure total chlorophyll and phycocyanin pigment (cyanobacteria) concentrations (https://www.bbe-moldaenke.de/en/). Pigment concentration measurements were taken in triplicate during sampling and averaged with the standard deviation calculated and reported in the results. TP concentration was measured on a HACH DR 3900 Spectrometer using the ascorbic acid method following digestion. Total microcystin concentration was measured by ELISA assay by the Celina Water Treatment facility. Ortho-P samples were filtered immediately upon collection (Fisher Scientific Target2 0.22 μm Nylon syringe filters) into 14 mL polypropylene test tubes (Karter Scientific), transported to the lab on ice (0–4 °C) and in the dark, and frozen at −20 °C. Ortho-P was analyzed using

Table 1. Mean values ± standard deviation for before, during, and after treatment in the lake and the enclosures. Matched pairs repeated measures T-test *p* values for each parameter across the entire sampling period (*p* values less than 0.05 are bolded)

Year	Total Phosphorus mg L^{-1}		Chlorophyll μg L^{-1}		Phycocyanin μg L^{-1}		Microcystins μg L^{-1}	
2020	Lake	Enclosure	Lake	Enclosure	Lake	Enclosure	Lake	Enclosure
Before alum (*n* = 10)	0.176 ± 0.042	0.214 ± 0.066	186 ± 116.4	108 ± 59.3	172 ± 116.4	96.3 ± 57.6	64.4 ± 20.4	52.1 ± 13.99
After alum (*n* = 19)	0.392 ± 0.123	0.339 ± 0.051	260 ± 57.7	206 ± 61.6	238 ± 59.8	163 ± 69.0	43.4 ± 16.58	28.0 ± 18.38
p Value	*0.9967*		***0.0013***		***0.0006***		***0.0101***	
2021	Lake	Enclosure	Lake	Enclosure	Lake	Enclosure	Lake	Enclosure
Before Phoslock + SeClear (*n* = 6)	0.166 ± 0.254	0.121 ± 0.093	36.7 ± 21.35	69.5 ± 35.4	18.1 ± 20.62	28.5 ± 33.6	2.70 ± 2.45	1.08 ± 1.53
During treatment period (*n* = 12)	0.142 ± 0.065	0.171 ± 0.072	121 ± 124.3	114 ± 87.6	88.6 ± 132.2	44.3 ± 55.6	1.71 ± 1.29	6.01 ± 15.52
Post treatments (*n* = 10)	0.310 ± 0.067	0.320 ± 0.036	283 ± 73.3	245 ± 31.9	270 ± 69.1	106 ± 46.6	5.09 ± 2.32	2.19 ± 1.25
p Value	***0.0318***		*0.5034*		*0.1018*		*0.5033*	

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colorimetric flow injection analysis (FIA) on a Lachat Quikchem 8500 (three injections per sample). Dissolved aluminum concentrations (only measured in 2020) were measured via inductively coupled plasma mass spectrometry (ICPMS).

Statistics

Differences in concentrations of environmental variables (variation in text and tables expressed as SD) between those measured at the untreated lake site and within the treated enclosure were compared using a matched pairs repeated measures T-test (JMP Pro v.17). In addition, evaluation of differences in concentrations of environmental variables before and after the single 2020 alum treatment within the enclosure were evaluated using ANOVA. Assumptions of normality and variance were assessed visually using histograms. Data that did not meet assumptions of normality were log-transformed prior to statistical analysis. All figures for these data were generated using the ggplot2 package in R (version 4.0.4, R Core Team, 2021) or JMP PRO 17.

Results

Alum treatments

The alum treatment in 2020 was originally planned for April/May 2020 but was delayed until June 9 due to the global pandemic. Chlorophyll, phycocyanin, and microcystin concentrations were 212 ± 2.6, 205 ± 2.1, and 45.6 μg L^{-1}, respectively, on the day before alum application (June 8, 2020). Chlorophyll and phycocyanin concentrations decreased to 74.0 ± 25.1 and 70.0 ± 24.1 μg L^{-1}, respectively, on the day of alum treatment. However, chlorophyll concentrations at the adjacent, untreated sampling station in the lake also decreased during this time (Figure 2). Two weeks after alum treatment (June 22, 2020), chlorophyll, phycocyanin, and microcystin concentrations within the enclosure were 255 ± 12.4, 244 ± 11.8, and 66.4 μg L^{-1}, respectively, representing increases concurrent with those observed in the lake (Table 1, Figure 2). Overall, chlorophyll, phycocyanin, and microcystin concentrations were higher (matched pairs repeated measures *T*-test, *p* values <0.05) in the lake than in the enclosure before and after the alum treatment (Table 1). However, the relative difference between the lake and enclosure narrowed during the post-treatment period indicating less relative differences between lake and enclosure. Moreover, average microcystin concentrations exceeded the WHO no contact advisory limit (24 μg L^{-1}) during the monitoring period.

Monthly ortho-P concentrations varied in 2020 (April through September), ranging from 0.46 to 12.2 μg L^{-1} inside the enclosure and from below the detection limit (~0.32 μg L^{-1}) to 154 μg L^{-1} outside the enclosure (Table S1). Higher ortho-P concentrations outside the enclosure coincided with low DO concentrations and a fish kill (Jacquemin and Cubberley, 2022). DO concentrations

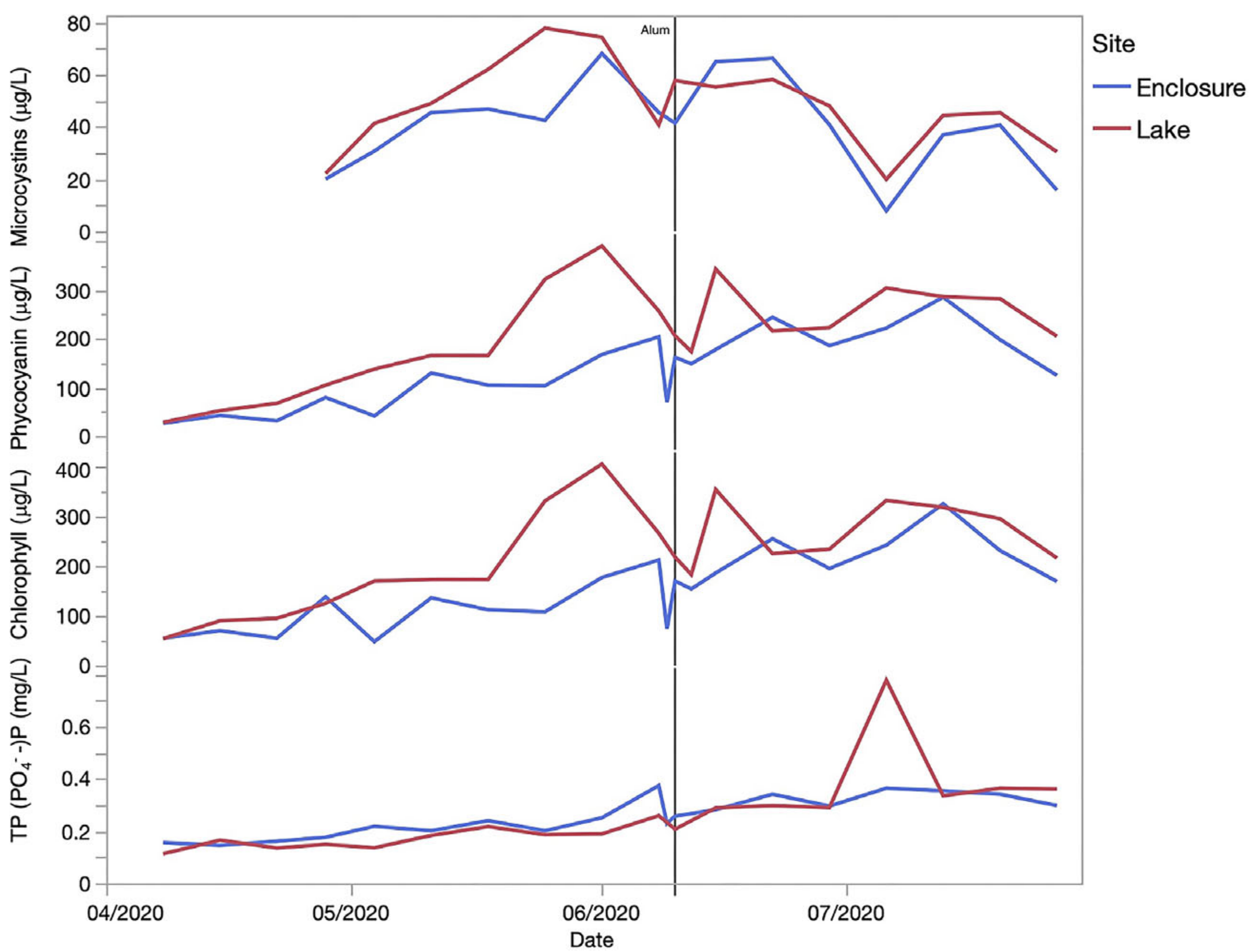

Figure 2. Total P, chlorophyll, phycocyanin, and microcystin concentrations before and after the alum treatment on June 9, 2020, within the enclosure (blue line) and within the lake nearby (red line).

varied over this first year monitoring period, ranging from 4.20 to 13.5 mg L^{-1} inside the enclosure and from 2.50 to 13.8 mg L^{-1} outside the enclosure (Table S1). DO concentrations decreased from 11.5 mg L^{-1} on the treatment day to 6.9 mg L^{-1} the day after treatment, concurrent with the visible decomposition of algal biomass. TP concentrations in the enclosure were 0.375 and 0.257 mg L^{-1} on June 8 and June 10, 2020, respectively, and increased in subsequent weeks (Figure 2). TP concentrations in the adjacent, untreated lake were 0.260 and 0.208 mg L^{-1} on June 8 and June 10, respectively. In the 2 months prior to the alum treatment, TP was higher in the enclosure than the lake (0.214 ± 0.067 mg L^{-1} vs. 0.176 ± 0.043 mg L^{-1}, respectively), but there was no difference in TP between the enclosure and lake across the sampling period (matched pairs repeated measures *T*-test, $p = 0.99$; Table 1, Figure 2). Dissolved aluminum concentrations did not change before or after the alum treatment within the enclosure (ANOVA, $p > 0.05$). In June, dissolved aluminum concentrations were similar in the lake and in the enclosure; however, concentrations decreased in the lake in July 2020, but not in the enclosure (Table 2).

Table 2. Dissolved aluminum concentrations (μg L^{-1}) in Grand Lake St Marys pre- and post-alum application (June 9, 2020)

Date	Enclosure	Lake
4/9/20	12.3	9.73
5/23/20	55.7	30.8
6/25/20	48.2	51.5
7/9/20	55.9	5.53

Lanthanum clay and algaecide treatments

In 2021, the enclosure received four treatments of Phoslock and SeClear (May 13, June 11, July 2, and August 13) and one treatment of SeClear only (July 23; Figure 3, SI Table 1). Total P and microcystin levels were slightly higher in the lake than enclosure while chlorophyll and phycocyanin values were higher in the enclosure than in the lake prior to the start of treatment (Table 1, Figure 3). In 2021, DO concentrations ranged from 4.40 to 11.7 mg L^{-1} inside the enclosure and from 2.7 to 12.4 mg L^{-1} outside the enclosure (Table S1). Ortho-P concentrations ranged from 1.5 to 3.8 μg L^{-1} inside the enclosure and from 1.3 to 2.6 μg L^{-1} outside the enclosure in 2021 (Table S1).

Immediately after the first Phoslock + SeClear treatment on May 13, chlorophyll and phycocyanin concentrations decreased to 14.5 ± 0.8 and 0.5 ± 0.1 μg L^{-1}, respectively, and DO decreased from 11 to 6.25 mg L^{-1}. These reductions in chlorophyll and phycocyanin persisted for about 1 week. On May 26, chlorophyll concentrations were 171 ± 2.4 μg L^{-1}, but phycocyanin and microcystin concentrations remained low (5.5 ± 0.7 and 0.3 μg L^{-1}, respectively), showing that non-cyanobacterial taxa dominated the phytoplankton community, as was also the case before treatment. TP concentrations the day

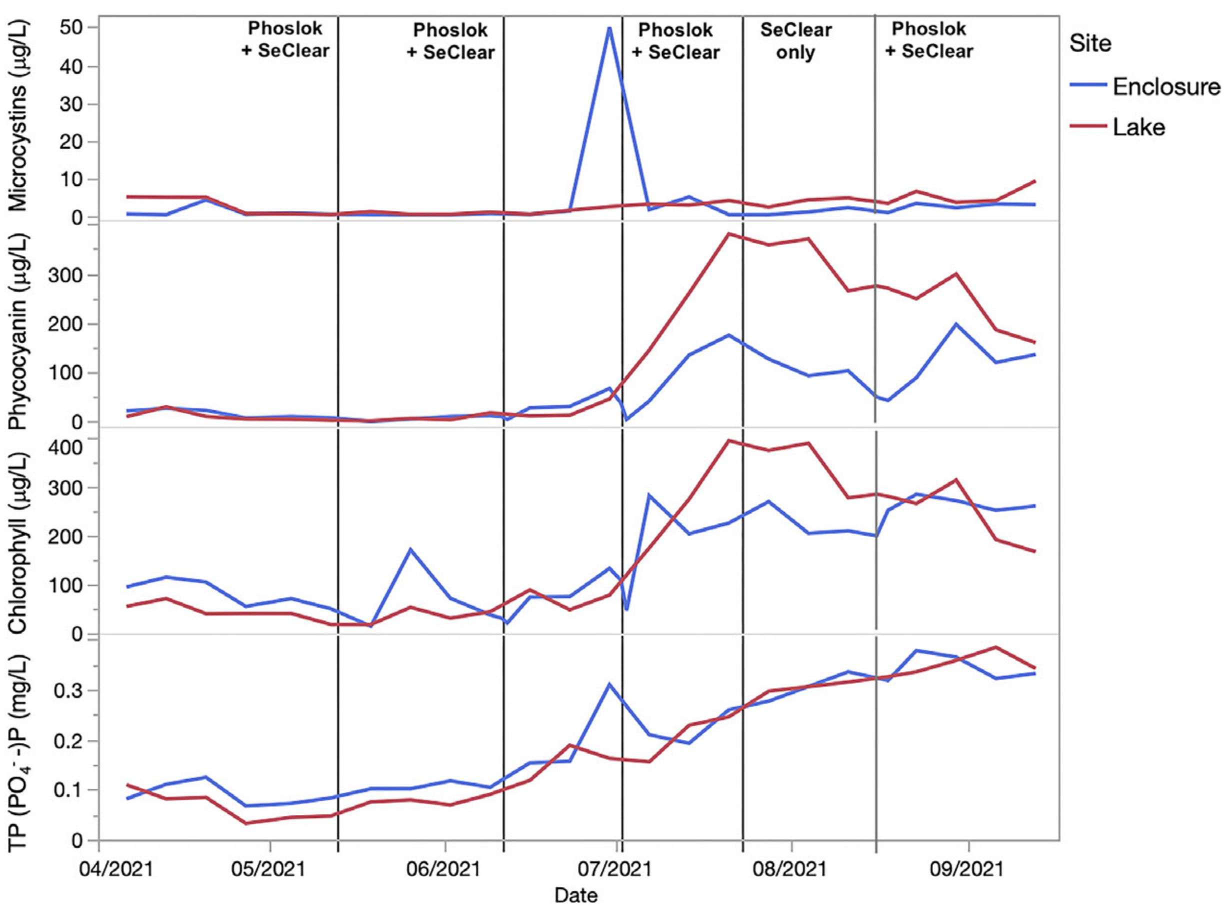

Figure 3. Total P, chlorophyll, phycocyanin, and microcystin concentrations before, during, and after the treatments (vertical lines) within the enclosure (blue line) and within the adjacent lake (red line).

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before treatment (0.101 mg L^{-1}) were similar to those a week after treatment (0.117 mg L^{-1}).

After the second Phoslock + SeClear treatment on June 11, 2021, TP, chlorophyll, and phycocyanin exceeded pre-treatment concentrations within days in both the enclosure and lake. Chlorophyll and phycocyanin concentrations in the enclosure immediately post-treatment were 39.0 ± 7.4 and 11.5 ± 2.5 μg L^{-1}, respectively, and 74 ± 3.1 and 28 ± 1.8 μg L^{-1} 5 days later. A similar pattern was observed in the adjacent lake.

After the third Phoslock + SeClear treatment on July 2, 2021, chlorophyll and phycocyanin concentrations decreased from 133 ± 15.8 and 68.2 ± 5.6 to 46.5 and 4.6, respectively, but quickly rebounded to 282 ± 15.6 and 42 ± 2.2 within 1 week. Microcystin concentrations before and after treatment were 2.4 and 1.6 μg L^{-1}, respectively. This treatment followed heavy precipitation, resulting in decreased conductivity, increased turbidity, and increased TP in the lake. The only high (50 μg L^{-1}) microcystin concentration in 2021 was observed in the enclosure in July, skewing the mean concentration during the treatment period.

The fourth treatment (SeClear only on July 23, 2021) exhibited chlorophyll, phycocyanin, and microcystin concentrations from 226 ± 0.9, 175 ± 0.9, and 4.0 μg L^{-1}, respectively, to 271 ± 4.7, 128 ± 0.9, and 0.3 μg L^{-1}, respectively, in the week following the treatment. After this fourth treatment, chlorophyll, phycocyanin, and microcystin concentrations were higher in the lake than enclosure (375 ± 4.1 μg L^{-1} for lake chlorophyll, 359 ± 5.6 for lake phycocyanin, and 2.3 μg L^{-1} for lake microcystin, p value <0.002; Table 1).

Prior to and after the fifth treatment (Phoslock + SeClear on August 13, 2021), lower phycocyanin and microcystin concentrations were observed in the enclosure for several weeks, but these values converged with those from the lake by mid-September. While phycocyanin decreased following this treatment, chlorophyll did not decrease, and both chlorophyll and phycocyanin increased 2 weeks later.

Concentrations of chlorophyll, phycocyanin, and microcystins were not different between the enclosure and the lake across the 2021 sampling period (matched pairs repeated measures T-test, $p > 0.05$; Table 1). Thus, no long-term impacts of the Phoslock + SeClear regime were observed beyond 4–5 weeks, with the most noticeable impact on chlorophyll lasting only ~2 weeks from the final treatment.

Discussion

This study evaluated the effectiveness of P-binding agents (i.e., alum, lanthanum-based clays, copper algaecide) to reduce TP concentrations and inhibit cHABs in a shallow, semi-enclosed area of hypereutrophic GLSM. Based on these evaluations, these technologies were not effective in this area of GLSM, although repeated applications of Phoslock + SeClear within the enclosure in 2021 temporarily reduced phycocyanin and microcystin concentrations. This study is further evidence that long-term, sustainable external loading reductions of both N and P from watersheds are preferable to short-term, expensive applications that may not be effective. Short-term treatments should only be used when combined with sustainable external nutrient (N and P) loading reductions, and only after a thorough system analysis is completed (Tammeorg et al., 2023).

The ineffectiveness of the alum treatment in this study was not surprising considering the ineffectiveness of previous alum treatments in GLSM, which were hypothesized to be due to high pH (Nogaro et al., 2013). One explanation for the failure of the alum treatment in 2020 was the late application date (June, originally scheduled for April) and the likelihood that bioavailable P was sequestered in biomass at the time of application (observed as low ortho-P and high TP); however, the Phoslock + SeClear treatments were also not successful beyond the day-to-week scale, even with lower chlorophyll concentrations prior to application and the earlier treatment date than 2020. Other alum treatments in shallow lakes impacted by frequent sediment resuspension have also exhibited only short-term impacts or been ineffective (Huser et al., 2016). Alum dosage, lake morphometry, and watershed-to-lake area ratios are key parameters related to treatment success and longevity (Huser et al. 2016). GLSM is very shallow (mean depth 1.5 m) with very high, non-point source external nutrient loads from an agricultural watershed (e.g., Steffen et al., 2014), making alum treatments unlikely to facilitate long-term benefits (Huser et al., 2016). Additionally, there is not enough data to conclude whether the alum treatment in the enclosure influenced aluminum concentrations remaining higher in the enclosure, but concerns about increased aluminum concentrations following previous alum treatments have been reported for GLSM (Nogaro et al., 2013).

Several studies have shown that using P-binding treatments alone, in systems with perennial cHABs and high external nutrient loading, is ineffective without also adding algaecide (Bacha et al., 2022; Lürling et al., 2022), which prompted decisions in 2021 to pair P-binding treatments of Phoslock with the algaecide SeClear. Phoslock is bentonite clay modified with lanthanum, and it binds phosphate rather than absorbing it, as alum does, potentially making it more effective in the long term (Zamparas et al., 2020). In 2021, repeated applications of Phoslock + SeClear within the enclosure had a measurable, but brief (a few weeks at best), impact on phycocyanin concentrations, but not chlorophyll (other than the first treatment) or TP. An unusually cold winter and lower spring nutrient loading preceded a milder bloom in spring/early summer 2021, with chlorophyll, phycocyanin, and microcystin concentrations at 50.0, 8.0, and 0.41 μg L^{-1}, respectively, on May 12, 2021, a day before the first Phoslock+SeClear treatment. Almost all measured microcystin concentrations in 2021 were below the WHO contact limit (24 μg L^{-1}), which has occurred only once in the preceding decade, also due to ambient environmental conditions rather than treatment (Jacquemin et al., 2023).

A meta-analysis of water quality in 18 lakes across Europe, 2 years after Phoslock treatment, reported decreases in TP, soluble reactive P, and chlorophyll across the systems (Spears et al., 2016). Similar results were reported in Laguna Niguel Lake (California, USA), after a whole-lake Phoslock treatment, and chlorophyll and TP concentrations remained lower 3—6 months post-treatment (Bishop et al., 2014). However, all but one of these lakes were deeper (>2 m) and had lower algal activity than GLSM. In the Spears et al. (2016) study, the 75th percentile values for chlorophyll decreased from 119 to 74 μg L^{-1}, and Secchi depth increased from 398 to 506 cm. In GLSM, chlorophyll in both the enclosure and lake remained above 200 μg L^{-1} after July 1, and Secchi depth never exceeded 30 cm. Another meta-analysis, including 12 Phoslock-only and five Phoslock + algaecide treatments, showed that both treatments temporarily reduced algal cell density (Anantapantula and Wilson, 2023). Phoslock and other physical treatments, including deep well circulation and dry-till, also did not improve water quality in terms of combined impacts on phytoplankton cell density, toxins, and off-flavor compounds (Anantapantula and Wilson, 2023). These findings support results from GLSM, where any positive effects of treatment did not persist for more than a few weeks.

Despite the engineering approaches to restrict water exchange between the enclosure and the lake to create a more easily treatable area, the treatment failures described here suggest that these approaches should not be repeated. These failures could be explained in part by water residence time in the enclosure, weather and runoff, algal biomass and treatment timing, failure to address bioavailable N, or any combination thereof. Our results suggest that P-binding and/or algaecide treatments would need to be conducted at least weekly. If the enclosure was not exchanging with the lake, and bioavailable N was not of concern, then two treatments of Phoslock + SeClear per year should be sufficient to treat the enclosure (Bishop and Willis, 2017). However, larger Phoslock doses, up to 200:1 (kg Phoslock:kg waterbody P, versus 50–80:1 used in GLSM), might be required to successfully reduce cyanobacteria in systems like the GLSM swimming enclosure. One dose of Phoslock + SeClear for the 3 ha area costs ~US$5,000, so weekly treatments from May through August would cost ~US$100,000 per year at the dosage applied in 2021. In addition, these treatments fail to address bioavailable N, which is required by *Planktothrix* and other non-N-fixing cyanobacteria to produce biomass and N-rich microcystins (Gobler et al., 2016; Newell et al., 2019). As suggested for western Lake Erie, failure to address external N loading could promote toxic strains of non-N-fixing cyanobacterial taxa (Gobler et al., 2016; Hellweger et al., 2022) and contribute to P-binding treatment failures.

GLSM is a large, shallow, hyper-eutrophic, polymictic lake with a large, agricultural watershed, making it a difficult system to treat, as shown by failures of previous P-binding treatments (Nogaro et al., 2013). Additionally, the residence time for GLSM can range from 150 to more than 500 days (Filbrun et al., 2013), favoring the proliferation of cyanobacteria (Hamilton et al., 2016; Steffen et al., 2014). P-binding treatments have been effective in some lakes, but results vary based on dosage, morphology of the treatment area, and water residence time (Huser et al., 2016). Correct dosages and applications depend on accurate estimates of P fluxes from sediments, and they do not address legacy N; thus, many treatment failures result from a lack of understanding of the system (Huser et al., 2016; Nogaro et al., 2013). Additionally, P-binding treatments may not improve, or may even negatively impact, water quality (Anantapantula and Wilson, 2023).

P-binding agents would be more effective in deeper, stratified lakes, with previous meta-analyses suggesting a 3–40 times difference in effectiveness compared with shallow, polymictic systems (Huser et al., 2016). Specific to GLSM and the dosage of alum applied, the decision tree and partition model of Huser et al. (2016) predicted that the treatment in the GLSM enclosure should have lasted 4.6 years. However, GLSM is shallow, well-mixed, and experiences frequent sediment resuspension, leading to a very low Osgood index value (0.0002); thus, the error associated with the Huser et al. (2016) model may have resulted in overestimated effectiveness. Results from the present study suggest that managers for lakes aligning with GLSM in physical and watershed characteristics should proceed with P-binding agents with caution and only after thorough system analysis (e.g., Lürling et al., 2023). Rather, funds available for applying P binding agents would be better invested in watershed conservation initiatives, such as reducing external nutrient loads (both N and P).

Conclusion

This study illustrates that chemical treatments aimed at reducing P concentrations, although effective in some cases, may not be effective in semi-enclosed areas of large, shallow, and hyper-eutrophic lakes. The combination of chemical treatments, linear aeration, sediment dredging, and attempts at reducing water exchange between the lake and enclosure did not prevent cHABs and toxin production. Initially positive results from these treatments, which cost USD$13,500 for alum application in 2020 and USD$32,350 for algacide/lanthanum treatment in 2021, did not persist. Previous chemical interventions with alum in GLSM were also not effective long term and demonstrated adverse effects on N cycling (including N_2O production and reduced denitrification), which would enhance, instead of inhibit, non-N-fixing cHABs, greenhouse gas release (Nogaro et al., 2013), and toxicity. Thus, the potential for long-term reductions in external nutrient (N and P) loads, such as implementing agricultural best management practices (BMPs) and the restoration or creation of wetlands within the watershed, should be the focus of lake managers for large, hypereutrophic, shallow lakes. Results in GLSM provide promising preliminary results for these approaches. In 2011, the State of Ohio declared GLSM as a distressed watershed, which led to obligatory nutrient management planning as well as manure management practices, and a series of voluntary conservation initiatives, which included the construction of treatment wetlands which have reduced external nutrient loads to GLSM in recent years (Jacquemin et al., 2023). Additionally, lower cyanobacterial biomass resulting from ice-over and reduced external nutrient loading in spring led to low microcystin concentrations in 2021 (Jacquemin et al., 2023), further highlighting the potential impact of reduced external nutrient loads.

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