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Ecological Engineering
Lürling, Miquel; Kang, Li; Mucci, Maíra; Oosterhout, Frank; Noyma, Natalia Pessoa et al
https://doi.org/10.1016/j.ecoleng.2020.106032

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Coagulation and precipitation of cyanobacterial blooms

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ARTICLE INFO

Keywords:
Geo-engineering
Lake restoration
Managing cyanobacterial nuisance
P control
Phoslock
Alum

ABSTRACT

Eutrophication is the prime water quality issue in inland waters. Eutrophication and its key symptom, harmful cyanobacterial blooms, is expected to further increase in the future, which highlights the importance of managing the issue. The reduction of external nutrient load is crucial but might not bring fast relief to eutrophic waters due to ongoing diffuse pollution and legacy nutrients in the sediment. In this context, in-lake measures are needed to speed-up recovery. In this review, we discuss different in-lake measures based on coagulation and precipitation of cyanobacteria and/or phosphate for different lake categories (e.g., shallow or deep, mainly external or internal nutrient load, occurrence of perennial or summer blooms). In deep lakes with an external nutrient load higher than the internal load, a “Floc and Sink” method could be used in which a coagulant (e.g. aluminium salts, Al-salts; chitosan) combined with a ballast (e.g. soil, clay) removes a cyanobacterial bloom out of the water column. In case the deep lake suffers from high internal load, a phosphate (P)-fixative (e.g. lanthanum modified bentonite or Al-salts) can be used to “Lock” the legacy P, possibly combined with a coagulant – a “Floc and Lock” technique. The latter approach will target both the particulate P in a bloom and the internal P load. A shallow lake that suffers from summer blooms and in which the internal load is higher than the external load, a “Lock” strategy of winter application of a P-fixative is proposed to prevent bloom development. In shallow lakes with perennial blooms, an agent to damage the cells (such as H\textsubscript{2}O\textsubscript{2}) is required together with a coagulant and a ballast to avoid recolonization of the water column due to resuspension – a “Kill, Floc and Sink/Lock” method. The selection of the most promising in-lake measures and materials should be based on a proper system diagnosis and tests prior to a full-scale intervention. These methods can be effective, but evidently reduction of external nutrient loads, both from point- and non-pointed sources, is an absolute necessity to restore aquatic ecosystems in a holistic sense.

1. Introduction

The over-enrichment with nutrients (i.e. eutrophication) of lakes, ponds and reservoirs is one of the most important water quality issues (Downing, 2014). Eutrophication may lead to drastic ecosystem changes, such as loss of submerged plants, a decrease in water transparency, an overgrowth of algae, increase of planktivorous- and benthivorous fish, an accumulation of organic matter and a large, recyclable sediment phosphorus (P) pool (Moss, 2010). The most notorious symptom of eutrophication is a massive proliferation of cyanobacteria (Paerl et al., 2011). Blooms of cyanobacteria are viewed problematic as they may produce nasty odours, cause fish kills due to hypoxia/anoxia, and may impair ecosystem services, such as drinking water production, irrigation, recreation, aquaculture and fisheries (Paerl and Paul, 2012). Eutrophication is expected to further increase in the upcoming decades because of human population growth, intensified...
agricultural activities and climate change (Cordell et al., 2009; Jeppesen et al., 2009; Moss et al., 2011; Sinha et al., 2017; Beaulieu et al., 2019). As a result, increased incidence, intensity and duration of cyanobacterial blooms in lakes, ponds and reservoirs are expected (Paerl and Huisman, 2008; O’Neil et al., 2012; Paerl and Paul, 2012; Huisman et al., 2018). Hence, mitigating eutrophication and controlling cyanobacterial blooms is of high importance to authorities and water managers.

The first step to counteract eutrophication is to reduce the external nutrient inputs (e.g., Hamilton et al., 2016; Paerl et al., 2016; Huisman et al., 2018). Targeting the cause of the problem is the most logical management strategy because a massive proliferation of cyanobacteria can occur only when all nutrients are abundantly available. Here, however, the wickedness of the problem is recognized, as it is already known for many decades that eutrophication fuels nuisance cyanobacterial blooms and therewith impairs water quality (Edmondson et al., 1956; Parma, 1980). Nonetheless, eutrophication is still a widespread problem (OECD, 2017), which illustrates the overall difficulty in adequate lowering of nutrient inputs into surface water. The impact of point source nutrient pollution, such as untreated wastewater, is already known since the 1950-ies and even in Europe, with the implementation of all sorts of policies over the past decades, improved wastewater treatment, discharge and storm water management is still needed in many countries (Ibisch et al., 2016). In low-income countries less than 10% of the municipal and industrial wastewater undergoes treatment of any kind (WWAP, 2017). Huge upfront investments will be needed in those countries to improve sewerage coverage and sewage treatment (van Loosdrecht and Brdjanovic, 2014). Tackling point sources such as wastewater effluents, however, gives no guarantee that eutrophication threats will vanish. In several cases, external point source load reduction did not yield the expected outcome and eutrophic conditions remained (Cullen and Forsberg, 1988), while in other lakes recovery was delayed by years to decades (Fastner et al., 2016), which is due to legacies and diffuse nutrient loads (OECD, 2014, 2017). For instance, urban wastewater treatment in the Netherlands is in full compliance with the Urban Waste Water Treatment Directive. Virtually all wastewater is treated and has 100% compliance for the elimination of nutrients (Coloma et al., 2017) and causethereleaseofintracellulartoxins (Paerl et al., 2016; Huisman et al., 2016a). The impact of diffuse nutrient sources is essential to restore aquatic ecosystems in a holistic sense (Steinman, 2019), however, they may involve many stakeholders and thus time before fully implemented, or there may simply be no space for such measures as in urbanized areas (Huser et al., 2016a). All in all, continued leaching from nutrient saturated soils in the catchment, recycling from nutrient-loaded sediments, together with changed biological make-up of eutrophic lakes will postpone improved water quality for decades to centuries (Jarvie et al., 2013; Rissman and Carpenter, 2015; Goyette et al., 2018). Consequently, a rapid diminishing of cyanobacterial blooms is not to be expected, unless in-lake interventions are implemented.

In-lake interventions encompass a great variety of different approaches, such as biomanipulation on fish and macrophytes, re- construction of the reservoir/lake, dredging, water column mixing, use of algaecides and so on (Lürling and Mucci, 2020). In this review, the focus is on the coagulation and precipitation of cyanobacteria and/or phosphate as promising tools to manage eutrophication and its nuisance.

2. In-lake measures

The cyanobacterial nuisance could be tackled immediately in many lakes using in-lake measures that would bring direct relief. Such interventions are particularly needed in situations where users of cyanobacteria infested waters simply have no time ‘to sit this one out’ or wait for many years until eventually external load control has been implemented and water quality improves. In-lake measures can be curative or symptom-oriented, such as flushing, mixing, targeting biomass, and/or preventative or source-oriented, such as increasing critical nutrient load level, lowering the nutrient load and improving water transparency via food web manipulations (reviewed in Stroom and Kardinaal, 2016; Lürling and Mucci, 2020).

The symptom-oriented interventions are intended to target the cyanobacteria directly. Direct targeting of cyanobacteria is commonly done cost-effectively with algaecides (Jančula and Maršálek, 2011). Copper-based algaecides are most frequently used to control nuisance algae (e.g., Iwinski et al., 2016), while novel algaecides are being developed to minimize unwanted side effects (Matthijs et al., 2016). Algaecides induce cyanobacterial cell lysis. Cell lysis may liberate nutrients (Coloma et al., 2017) and cause the release of intracellular toxins (Jones and Orr, 1994; Jančula and Maršálek, 2011).

Alternatives to cell-lysing algaecides are interventions based on coagulation, flocculation and removal of cyanobacterial biomass. Here, the use of mineral/metal-based, natural, organic and synthetic coagulants (Lee et al., 2014) can be considered to aid aggregation, flotation and dewatering (e.g., http://waterned.com/), or when combined with a ballast to effectively sink the aggregates to the sediment – a “Floc and Sink” approach (Fig. 1A) (Pan et al., 2011a; Lürling and Oosterhout, 2013; Waajen et al., 2016a). Such interventions can immediately swipe a water column clear of cyanobacteria without releasing toxins and nutrients. This type of intervention seems best suited for deep, stratifying lakes with ongoing external nutrient load, as the cyanobacteria can be removed effectively from the epilimnion and brought to the sediment (Fig. 1C). External load control is an absolute necessity in those waters, where in-lake measures such as biomanipulation could be implemented to speed-up recovery. Otherwise, both in a perennial blooms scenario or recurring summer blooms, repeated use of algaecides such as hydrogen peroxide might be an option (Matthijs et al., 2016). In shallow lakes with low external load, but a relatively large internal load, preferably the cyanobacteria are killed first before settled to the sediment (Fig. 1D). Alternatively, only a P-fixative is used before the growing season taking away the fuel for the blooms.

3. ‘Floc and Sink’ of cyanobacteria

In marine systems, algae can be precipitated using a clay as a single measure (Sengo et al., 2001; Deng et al., 2015). In contrast in freshwater, solely adding clay or other ‘ballast compounds’ will hardly lead to the removal of cyanobacteria as net electrostatic repulsive force between negatively charged clay particles and cyanobacteria prevent collision (Noyma et al., 2017), unless the cyanobacteria themselves are sticky (Verspagen et al., 2006). Consequently, efficient removal of
cyanobacteria in freshwater systems can only be achieved by the combination of a dose of coagulant and a ballast (Pan et al., 2006; Zou et al., 2006; Noyma et al., 2016). In this so-called “Floc and Sink” technique (Noyma et al., 2016), different coagulants and ballast compounds can be used that – before being applied at a specific site – need to be tested in a laboratory-based “Floc and Sink” assay first to yield insight on their performance and dose needed (Fig. 2).

Coagulants can be metal-based, such as aluminium sulphate (alum),
poly-aluminium chloride (PAC) and iron(III)chloride (Pan et al., 2011a; Lürling and Oosterhout, 2013; Waajen et al., 2016a; de Lucena-Silva et al., 2019), organic polymers like chitosan (Pan et al., 2006, 2011b; Noyma et al., 2016, 2017) and cationic starch (Shi et al., 2016), synthetic organic coagulants like cationic polyacrylamides (Jančula and Maršálek, 2011) and cationic polyamine (Dai et al., 2015), or extracts derived from Moringa oleifera seeds (Oladoja and Pan, 2015; Camacho et al., 2017; de Oliveira Ruiz Moreti et al., 2019).

Ballast compounds may be local soils, clay, bauxite, gravel (e.g., Pan et al., 2006, 2011a; Li and Pan, 2015; Noyma et al., 2016, 2017; Miranda et al., 2017; de Lucena-Silva et al., 2019), or modified clays and products with P adsorption capacity (e.g., Lürling and Oosterhout, 2013; Noyma et al., 2016, 2017; Waajen et al., 2016a). The latter is a special case of “Floc and Sink” (Noyma et al., 2016) as it is also aimed at removing phosphate from a water column and reducing sediment P release: a “Floc and Lock” approach (Lürling and Oosterhout, 2013), which will be discussed in detail in the next section.

The choice of coagulant and ballast compounds will be based on safety, costs, availability and efficacy. Testing selected combinations with water from the specific site is required as a priori determination of coagulation efficiency and best dose is impossible (Figs. 2 and 3). Removal efficacy between 88% and 99% removal could be reached (Noyma et al., 2017). At higher cyanobacterial biomass, more ballast is needed to achieve good removal (Noyma et al., 2017). This efficient removal of cyanobacteria by combining a low dose of coagulant and ballast can be achieved without changing the cell surface charge or zeta potential (Noyma et al., 2017). The coagulants bridge between particles, create flocs that entrap cyanobacteria and subsequently sweep through the water column entrapping more cyanobacteria cells (Huang and Chen, 1996; Yu and Somasundaran, 1996; Li et al., 2013; Yang et al., 2016; Noyma et al., 2017).

Coagulation efficacy depends on several factors such as species-specific characteristics (Lama et al., 2016), temperature (Xiao et al., 2008), mixing intensity (Du et al., 2020) and water chemistry as not all coagulants are equally suited in all water types (Lürling et al., 2017). The pH of the water seems to affect coagulation efficiency of most coagulants. Chitosan was most effective at pH below 8 (Lürling et al., 2017), but was not an effective coagulant at elevated pH 9–10 (Moraes et al., 1985; Vandamme et al., 2013). Alum was most effective at pH 5–9, while lime with magnesium could effectively flocculate algae at pH 10–11 (Friedman et al., 1977). Comparing the efficacy of four coagulants in removing M. aeruginosa in water from Lake Dianchi (China) yielded that alum and iron sulfate were effective in a pH range from 6 to 8, while PAC and polymeric iron sulfate (PFS) were effective in pH range of 5 to 8 (Ma et al., 2015). At pH 9, alum still removed 70% and the other three coagulants removed 78–82% of the M. aeruginosa (Ma et al., 2015).

Because hydrogen ions are released during hydrolysis of aluminium-based coagulants, they may cause a decline in the pH of lakes and buffers may be needed (Cooke et al., 2005). PAC causes less pH reduction than alum and also has the advantage that a lower dose is needed, and better coagulation is achieved at lower temperatures (Gebbie, 2001; de Julio et al., 2010).

Application of aluminium formulations (PAC, alum) in waters with pH 6–8 is generally considered safe (Cooke et al., 2005; Jančula and Maršálek, 2011) and generation of toxic aluminium species - positively charged ions at pH < 5.5 and negatively charged aluminate at pH > 8.5 - is not to be expected (see Fig. 8.1 in Cooke et al., 2005). Nonetheless, potential issues in this pH range cannot be excluded, such as suffocation of fish by polymerized aluminium (Poléo, 1995), weight loss of fish and short-term effects on macrofauna (Smeltzer et al., 1999). Hence, environmental friendliness of metal-based coagulants has been questioned, with the promotion of organic, degradable coagulants such as chitosan as a “biodegradable, non-toxic material” (e.g., Renault et al., 2009). Chitosan, however, has antibacterial, antimicrobial, and antifungal activities (e.g., Kong et al., 2010; Younes et al., 2014), leading to bacterial cell membrane damage (Liu et al., 2004). Indeed, chitosan caused cell membrane damage in several cyanobacteria (Mucci et al., 2017), causing cell leakage (Pei et al., 2014) and leakage of cyanotoxins in field samples dominated by Cylindrospermopsis raciborskii (Miranda et al., 2017). Inasmuch as coagulated cyanobacteria may otherwise stay alive, chitosan induced cell lysis could decrease the chance of recolonization of the water column and, thus, is not per se a drawback (Mucci et al., 2017).

Chitosan is the preferred coagulant in the “modified local soil induced ecological restoration” (MLS-IER) technology in which local soil (near the bank of a lake) can be modified by adding a small amount of biodegradable coagulant (Pan et al., 2011b). The MLS-IER method combines both removal of phytoplankton biomass and conversion of their nutrients into submerged macrophytes (Pan et al., 2011b). The

Fig. 3. Testing combined coagulant (PAC + red soil) in enclosures in Mapro Lake (Museu Mariano Procópio), Juiz de Fora (Brazil), September 2016. Panel A: Dr. Felipe Pacheco dosing red soil. Panel B: the effect after one day. Panel C: a control enclosure. Panel D: a treated enclosure.
combination can be effective in settling cyanobacteria, lowering algal resuspension, reducing nutrient fluxes, and decreasing microcystins release from settled flocs (Li and Pan, 2015; Pan et al., 2012). Moreover, the coagulation-capping treatment may promote cell lysis and stimulate submerged macrophyte growth (Zhang et al., 2018). The latter is of crucial importance in shallow water bodies where a shift from a phytoplankton dominated state to a macrophyte dominated state is desired (Scheffer et al., 1993). This has occurred in a field trial in Liaoayangyuan bay (North Taihu Lake, China), where treatment of the 0.1 km² bay with 40–50 g MLS m⁻² removed the cyanobacteria bloom and promoted growth of the macrophyte Potamogeton crispus in a few months to densities of 1 kg m⁻² (Pan et al., 2011b). Treatment of a 400 m² pond in Taixi bay (China) with 16 kg of chitosan-MLS (i.e. 40 g MLS m⁻²) strongly reduced chlorophyll-a concentrations and nutrients and improved transparency from 5 cm to 1.5 m (Pan et al., 2019). Likewise, treatment of an 800 m² pond in Cetian Reservoir (China) with 32 kg of chitosan-PAC MLS improved water quality and yielded a macrophyte coverage of 65% after four months (Pan et al., 2019). A switch to a clear water state with submerged macrophytes can, however, only be achieved when the nutrient load is below the upper critical level for the transition from clear to turbid water (see Fig. 7). In addition, the fetch is of great importance as settled flocs could be resuspended. For instance, Huang et al. (2015) reported that cyanobacteria derived material, which was settled with chitosan modified clay, was resuspended at a shear stress of 0.109 Nm⁻² that corresponds to a low wind velocity of around 3.4 m s⁻¹. Those authors prevented resuspension by adding sand, however at a dose of 14 kg m⁻², which equals 140 ton ha⁻¹ (Huang et al., 2015), and implies such capping will become economically unfeasible. Consequently, wind effects constrain the application of a “Floc and Sink” approach in wind-exposed, large, shallow lakes (Fig. 1C).

4. ‘Floc and Lock’ of cyanobacteria and phosphate

The term “Floc and Lock” describes interventions in which cyanobacteria are aggregated and transported to the sediment in flocs (“Floc”), whilst water column phosphate and sediment phosphate release are reduced by chemical binding (“Lock”). This can be done by combining a coagulant and a P fixative as ballast or by using an aluminium salt as coagulant and P binder.

4.1. Geo-engineering using aluminium salts

When aluminium sulphate (alum) or poly-aluminium chloride (PAC) are added to the water column, Al(OH)₃-flocs are formed to remove dissolved P from suspended particles. Such water clearing effect was already demonstrated in the first alum treatment. Ten tons of granular alum were added to the Swedish Lake Långsjön in early summer 1968: transparency improved immediately from a few dozens of cm to a visible bottom (3 m), total P was reduced by 95% and for the first time in decades no cyanobacterial bloom formed (page 68 in Butusov and Jernelöv, 2013). Since the first application in Lake Långsjön hundreds of lakes have been treated with alum of which most were successful in blocking the release of mobile P from sediments (Cook et al., 2005). Similar results can be obtained with PAC. For instance, addition of PAC to the hypereutrophic Lake Sønderby (Denmark) caused a 93% reduction in the internal P loading in the two post-treatment years relative to pretreatment internal P loading (Reitzel et al., 2005).

A meta-analysis on 114 alum treated lakes revealed improved water quality with a mean treatment longevity of 21 years in deeper, stratified lakes and a mean of 5.7 years in shallow, polymeric lakes (Huser et al., 2016b). Sediment disturbance by bottom-feeding fish (carp) was identified as a major factor reducing the longevity of the treatment in shallow lakes (Huser et al., 2016b), because already moderate densities of carp can increase the sediment mixed layer from 5 cm without carp to 16 cm with carp, which may liberate a large pool of mobile sediment P to the water column (Huser et al., 2016c). In addition, Al(OH)₃-flocs are fluffly and are easily resuspended and redistributed (Egemose et al., 2010). When the Al flocs are resuspended into the water with a pH above 8.5, flocs may dissolve, form aluminate-ions and release P (Van Hullebusch et al., 2003; Reitzel et al., 2013a).

In lake restoration with aluminium compounds, mostly alum (Al₂(SO₄)₃·18H₂O) has been used (Cook et al., 2005), which contains sulphate. Adding substantial amounts of sulphate to surface waters, however, may stimulate internal eutrophication, because bacteria may transform sulphate to sulphide that subsequently attacks iron in iron-P minerals in the top sediment forming pyrite and mobilising P (e.g., Smolders et al., 2006). Alum can be dosed in a one-time application, a “shock and awe approach”, aimed to inactivate all mobile P in the top sediment (Cook et al., 2005). Such approach has a higher risk of undesired side effects that may be lowered by repeated lower dose applications, which may also reduce the loss of P adsorption capacity as aluminium flocs start to age once formed (e.g., de Vicente et al., 2008).

Despite the fact that aluminium-based treatments tackle water column P, mobile P in the sediment and have an instantaneous positive effect on water transparency, potential side effects stimulated search of water authorities and lake managers for alternative P fixatives that should be effective and safe (Spears et al., 2013a; Douglas et al., 2016). These P-fixatives are referred to as geo-engineering materials, which are used to manipulate biogeochemical processes to achieve a desired chemical and/or ecological response (Spears et al., 2014). A wide variety of geo-engineering materials exists that can be divided into four categories: 1) naturally occurring minerals or soils, 2) natural or synthetically produced materials, 3) modified clay minerals or soils, and 4) mining, mineral processing and industrial by-products (Douglas et al., 2004, 2016; Spears et al., 2013a). A detailed overview of the most important representatives of P-adsorptive materials in each category is provided by Douglas et al. (2016). In a “Floc and Lock” context, the lanthanum modified bentonite (LMB) Phoslock® has been applied (Lürling and Oosterhout, 2013; Waajen et al., 2016 a,b).

4.2. Geo-engineering using LMB

LMB was developed by CSIRO in 1990-ies (Douglas, 2002) and some years later made commercially available as Phoslock®. LMB is a bentonite clay which is enriched up to a 5% mass fraction with lanthanum as active ingredient via an exchange of cations in the clay interlayers (Douglas, 2002; Douglas et al., 2004). Lanthanum is not redox sensitive and has strong affinity for phosphate with which it precipitates as the LaPO₄ mineral - rhodophane (Ksp = 10⁻²⁴.⁷ to 10⁻²⁵.⁷mol²l⁻²) (Johannesson and Lyons, 1994; Liu and Byrne, 1997). Rhodophane is stable at least in the pH range 5–9 (Copetti et al., 2016); LMB showed excellent phosphate removal when tested in the pH range 6–9 (Mucci et al., 2018).

Meanwhile, LMB has been applied in around 200 water bodies worldwide (Copetti et al., 2016). These waters range from golf course ponds, in which P and cyanobacteria blooms could be reduced drastically (Bishop and Richardson, 2018), to larger lakes like the 130 ha Lake Goldap, Poland (Lürling et al., 2020). Application doses ranged from as low as 0.1 t LMB ha⁻¹ to as high as 6.7 t LMB ha⁻¹ (Spears et al., 2013b). A detailed overview of the scientific knowledge on LMB to manage eutrophication in surface waters has been published by Copetti et al. (2016). That review wraps together data of extensive testing at laboratory, mesocosm, and whole lake scales. A meta-analysis on 18 LMB treated lakes revealed greatly improved water quality in two
years post-application compared to two years pre-application (Spears et al., 2016). High-resolution dialysis (HR-Peeper) and diffusive gradients in thin films (DGT) confirmed that mobile P was strongly reduced by LMB in sediment (Wang et al., 2017), while sediment core incubations showed a strong reduction of the sediment P release after LMB dosing (Waajen et al., 2016b). Sediment analysis of 10 LMB treated lakes by $^{31}$P MAS NMR and La LIII EXAFS spectroscopy confirmed rhabdophane (LaPO$_4$·$n$H$_2$O) and to lesser extent monazite (LaPO$_4$) was formed (Dithmer et al., 2016), which are highly resistant rare earth phosphate minerals (Douglas et al., 2004). Since these minerals will not release any P under normal natural conditions (Douglas et al., 2016), it provides solid proof of permanent inactivation of P in those sediments.

LMB can remove phosphate as efficient in brackish water (1.5–15 ppth) or seawater (32 ppth) as in freshwater (Reitzel et al., 2013b; Bishop et al., 2014; Mucci et al., 2020) and reduce sediment P-release (de Magalhães et al., 2019). However, analysis of LMB in water of 4 ppth and 32 ppth revealed pushing out of La from the clay interlayers, forming La-oxyanion precipitates, which may hamper its applicability in saline environments when dosed from the water surface (Mucci et al., 2020). La leaching has also been observed in low alkalinity waters, which seems to be mostly facilitated by complexation of La with humic acids (Reitzel et al., 2017). All in all, exposure to LMB treated water is unlikely to pose a health risk to animals and/or humans (D’Haese et al., 2016; Behets et al., 2020) and to date, no indications for long-term negative effects on LMB-treated ecosystems have been found (Copetti et al., 2016; Van Oosterhout et al., 2020a).

4.3. Geo-engineering using coagulants and LMB

The first application of LMB combined with PAC as coagulant was done in the Dutch bathing site Lake Rauwbraken (Lürling and Oosterhout, 2013; van Oosterhout et al., 2020a, 2020b; Fig. 4). Lake Rauwbraken (2.6 ha, max. depth 15 m) suffered from intensifying cyanobacterial blooms culminating in a four-month swimming ban in 2007. In April 2008, the developing bloom was terminated effectively by using a coagulant (PAC, 1.1 mg Al l$^{-1}$) and 2 tons of LMB as ballast that was added from a barge and aggregated and settled the cyanobacteria (Fig. 4A). Besides an immediate settling out of the cyanobacteria, the intervention reduced the chlorophyll-a concentration from an average of 16.5 μg l$^{-1}$ before to 5.5 μg l$^{-1}$ after the intervention and total-P from 134 μg l$^{-1}$ to 14 μg l$^{-1}$ for more than 10 years (van Oosterhout et al., 2020b; Fig. 4B).

Before the 2008 intervention, internal loading (5.0 mg P m$^{-2}$ d$^{-1}$) made up 80% of the total P load (6.2 mg P m$^{-2}$ d$^{-1}$). Internal P load was reduced to 1.8 mg P m$^{-2}$ d$^{-1}$ in 2011, while the external P-load had increased from 1.2 mg P m$^{-2}$ d$^{-1}$ before 2008 to 1.4 mg P m$^{-2}$ d$^{-1}$ in 2011 (van Oosterhout et al., 2020b). Because the main external P load sources (water birds ~0.7 mg P m$^{-2}$ d$^{-1}$, leaf litter ~0.35 mg P m$^{-2}$ d$^{-1}$, groundwater ~0.2 P m$^{-2}$ d$^{-1}$) are difficult to control, repeated interventions will be required to maintain an acceptable bathing water quality. The system-analysis, more specific the cost-benefit analysis of it, underpinned that the treatment costs of € 50,000,- were far less than the € 150,000,- costs from a loss of revenue (visitors pay an entrance fee) of the four months swimming ban in 2007 prior to the intervention (pers. comm. Jan Hamming; alderman of Tilburg municipality). The entrance fee is € 5.50 per visit nowadays (https://derauwbraken.nl/strandbad/, assessed April 8th 2020). Given that the “Floc and Lock” treatment of Lake Rauwbraken created good water quality since its application in 2008 (van Oosterhout et al., 2020a, 2020b; Fig. 4B), the annual costs for improved water quality boil down to around € 4000,- per year, which is less than 5% of the fee per visitor to Lake Rauwbraken. Hence, this intervention was cost-effective. Repeated LMB interventions would be the most logic; once every decade seems reasonable for this lake, which implies annual costs lower than

Fig. 4. ‘Floc and Lock’ treatment in Lake Rauwbraken (the Netherlands) in April 2008 using 2 tons of PAC (1.1 mg Al l$^{-1}$) and 2 tons of LMB (Phoslock®) as ballast followed by 16 tons LMB as sediment P-fixative. Panel A: a surface application using a barge. Panel B: long term total-P concentrations two years before (mean 134 μg l$^{-1}$) and ten years after the intervention (mean 14 μg l$^{-1}$).
the maintenance of the beach.

Another “Floc and Lock” example is Lake De Kuil, a 6.7 ha, maximum depth 9 m sand excavation used as swimming lake. The lake was treated with 4.38 tons FeCl3 as a coagulant, 13.65 tons LMB as ballast (determined in jar tests prior to the intervention), while 28.25 tons of LMB were injected in the hypolimnion to target sediment P release (Waajen et al., 2016a). The LMB dose was based on water column P and potential releasable P in the top 5 cm of the sediment yielding 465 kg P that needed to be immobilized (Waajen et al., 2016a). This “Floc and Lock” intervention (cost € 140.000) effectively precipitated a developing cyanobacterial bloom and shifted the lake from a eutrophic to a mesotrophic state, which lasted for eight years (Waajen et al., 2016a) and came down to less than € 1.50 per visitor. The lake has been without swimming bans and was retreated in May 2017 to counteract ongoing diffuse P-load. 10.05 tons of ballast LMB were added to the water surface followed by 6 tons PAC as a coagulant and thereafter 22.05 tons of LMB were injected into the hypolimnion. The authorities decided to execute a reappraisal of ~€ 100.000, because it was most cost-effective. Bartoszek and Koszelnik (2015) mentioned treatment of Jelonek and Winiary lakes (Poland) with an injection of PIX 111 as a coagulant (FeCl3) and LMB directly into the sediment. However, the effectiveness of this application is not yet known.

5. Problem diagnosis and lake type characterization

Not a single water body is an exact copy of another and, thus, “each lake has to be studied before restoration measures can be applied” (Van Liere and Gulati, 1992). This means that a proper system analysis - deciphering the water and nutrient fluxes and therewith the nutrient loading of the water body, as well as its biological characteristics - should always be conducted before implementation of measures, as it will indicate what kind of measures will be most promising (Cooke et al., 2005; Lürling et al., 2016a; Stroom and Kardinaal, 2016). Reality is, however, quite different; only in a few cases has the choice for specific measures been explained (Stroom and Kardinaal, 2016) and copy-paste of measures seems more a rule than an exception. For instance, the majority of lake restoration (bio-manipulation) projects in The Netherlands failed, because of neglecting in-lake nutrient loading (Gulati and Van Donk, 2002), which implies no system analysis had been conducted.

The system analysis will identify if external nutrient load, internal load or both are driving cyanobacterial nuisance, or if the nuisance is merely caused by physical accumulation on leeside shore of otherwise low water column dispersed biomass. In situations where the external nutrient load is the main issue, reduction of external nutrient inputs is the most logic first management strategy (e.g., Hamilton et al., 2016; Paerl et al., 2016; Huisman et al., 2018). Without additional in-lake measures, however, recovery is predicted to take decades to centuries (Sondergaard et al., 1999; Carpenter, 2005; Cooke et al., 2005). To control outbreaks of cyanobacterial blooms in deep lakes, stratifying lakes a “Floc and Sink” approach can be considered (Fig. 5A). Cyanobacteria can be brought to the sediment, leaving a clear and low nutrient epi- limnion until the external load has reloading it allowing re-establish- ment of the bloom (Fig. 1). In contrast, in large, shallow, wind-exposed lakes, coagulation and sinking will be of limited to no-use as flocs are easily resuspended and cyanobacteria liberated (Fig. 5B). In smaller, shallow lakes, a “Floc and Sink” approach can be considered, but only when cyanobacteria are killed to reduce the possibility of recoloniza- tion of the water column (Fig. 5B). This “Kill, Floc and Sink” combi- nation has been tested in a laboratory setting using hydrogen peroxide as algaeicide, polymeric ferric sulphate as a coagulant, lake sediment as ballast (Wang et al., 2012), and with calcium peroxide as an algaeicide, chitosan as a coagulant and red soil as ballast (Noyma et al., 2014). To our knowledge, the only in situ test has been performed in an enclosure experiment in Juiz de Fora (Brazil) using hydrogen peroxide as algae- cide, PAC as coagulant and red soil as ballast (unpublished). Hydrogen peroxide will damage the cyanobacteria and nutrient release from the lysed cells may stimulate regrowth; a ballast with P-binding properties could be considered. Clearly, these symptom-oriented, in-lake measures are far from ideal, cannot be implemented in each lake type, need to be repeated regularly and, thus, should not only be effective and safe but also be cheap.

In deep, stratifying lakes with a relatively large internal load, strong reduction of the sediment P release could be a strategy for (speeding up) recovery. Dosing a P-fixative before the growing season, or combined with a coagulant during growing season, or when the lake suffers from perennial blooms could be considered (Fig. 5A). In a large, shallow lake, a P-fixative that keeps binding capacity until all binding site are occupied could be considered. Even when resuspended, ongoing P removal would imply strong competition with cyanobacteria. In case, cyanobacteria abundance is relatively high, P from the cells needs to be liberated first (Fig. 5B). In smaller, shallow lakes, immobilizing P before the growing season, combined with bottom resuspension fish removal and macrophyte introduction could be a promising strategy. Such combination of measures has been tested in 400 m² compartments in 2009–2011 (Waajen et al., 2016b; Fig. 6) and a “Lock and Grow” ap- proach with planting charophytes following a PhoslocK® treatment has been executed successfully in the small Lake Reithersee (Reith im Alpbachtal, Austria) (Epe et al., 2020).

The rationale for combined measures is rooted in the feedback mechanisms that stabilise alternative states in shallow lakes: the turbid, phytoplankton-dominated state and the clear water state with sub- merged macrophytes (Scheffer et al., 1993; Fig. 7). The transitions from clear to turbid and from turbid to clear occur at different nutrient loadings due to state self-enforcing mechanisms (Scheffer et al., 1993). Nutrient loadings need to be reduced much further to enforce a shift to clear water than at which the water became turbid (Fig. 7). However, when bottom-resuspending fish (bream, carp) are abundant in densities of hundreds of kg per hectare (Waajen et al., 2014), the water will remain in a turbid state by resuspending sediments and preventing submerged macrophyte establishment (e.g., Cline et al., 1994; Roosen et al., 2007). Consequently, fish density should be reduced to preferably less than 50 kg per hectare (Gulati and Van Donk, 2002) and macrophyte introduction could be considered. Measures that do not reduce the nutrient load to below the upper transition (from clear to turbid water), will at best only temporarily alleviate cyanobacterial nuisance (Fig. 7) and, thus, repeated interventions are needed to control cy- nobacterial blooms in such high nutrient load systems (Fig. 5). The needed curative interventions should be effective, easy, safe and af- fordable (Table 1).

Special cases are oligo- and oligo-mesotrophic lakes where the cy- nobacterial nuisance is caused by an accumulation of cyanobacteria present in low amounts in the water column. Direct targeting of the accumulation seems the most straightforward intervention (Fig. 5A). This is usually done applying algaeicides (Jančula and Maršálek, 2011; Matthijs et al., 2016). The algaeicide treatment could be followed by a coagulant/ballast dose to bind cyanotoxins and nutrients released from killed cells (Kill-Floc/Sink/Lock approach). For instance, combined chitosan-nano scale montmorillonite not only effectively precipitated Microcystis aeruginosa cells (94% removal), but also removed 90% of the extracellular microcysts within one hour (Wang et al., 2015). Like- wise, LMB (50, 100, and 150 ppm) decreased microcystin concentra- tions by 61.2, 86.0, 75.4% relative the controls, respectively (Laughinghouse IV et al., 2020).

6. Widespread application of geo-engineering in lakes, ponds, and reservoirs

Hundreds of aluminium based treatments have been performed in lakes varying from a few to several hundreds of hectares in size as well as in small ponds (Cooke et al., 2005; Huser et al., 2016b). LMB has been applied to over 200 lakes up to a few dozens of ha (Spears et al.,
and recently also LMB additions to the 250 ha sized Lagoa da Pampulha (Brazil) have been started. These applications illustrate that geo-engineering interventions will be particularly powerful in smaller sized water bodies. A lot of those small-sized stagnant water bodies are close to urbanized areas and are of great importance to societies (Waajen et al., 2014). Since small water bodies
are relatively easy diagnosed, they could make good candidates for geo-engineering to improve water quality (Waajen et al., 2016b; Fig. 6). Large lakes with relatively high external nutrient load can only be protected by lowering the external nutrient load because in-lake measures in waterbodies of thousands of km² will be impractical and too expensive (Paerl et al., 2016). In some cases, however, compartmenting (Stroom and Kardinaal, 2016) and using within-compartment measures could be a strategy for nuisance control. Compartmenting might provide an engineering solution to drinking water issues for instance in a created compartment, but it will not solve eutrophication issues in the large lake.

Resuming, a lake system analysis is key; it will elucidate the main drivers of the cyanobacterial nuisance and assist in designing tailor-made solutions. External load reduction is of paramount importance, but in the majority of cases also in-lake interventions will be needed. Watershed or catchment activities aimed at reducing the nutrient leakage to surface waters may take too long to be implemented, may be less effective than assumed and may take decades to centuries until effects become visible (Jarvie et al., 2013; Rissman and Carpenter, 2015; Goyette et al., 2018). In-lake measures may reduce nuisance and/or speed-up recovery, the most promising strategy will follow from the diagnosis. “Floc and Sink” strategies using an appropriate coagulant and ballast compounds can remove cyanobacteria effectively from the

Table 1

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Price (USD per ton)</th>
<th>Ballast</th>
<th>Price (USD per ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum</td>
<td>130–200</td>
<td>Sand (sieved)</td>
<td>100–200</td>
</tr>
<tr>
<td>PAC</td>
<td>200–400</td>
<td>Kaolinite clay</td>
<td>170–400</td>
</tr>
<tr>
<td>Fe(III)Cl₃</td>
<td>200–500</td>
<td>Bentonite clay</td>
<td>100–200</td>
</tr>
<tr>
<td>Cationic starch</td>
<td>200–600</td>
<td>Zeolite</td>
<td>150–300</td>
</tr>
<tr>
<td>Chitosan</td>
<td>1000–95,000</td>
<td>Al modified zeolite</td>
<td>2700</td>
</tr>
<tr>
<td>Polyacrylamide</td>
<td>1200–3000</td>
<td>La modified bentonite</td>
<td>2000–2500</td>
</tr>
</tbody>
</table>

Fig. 6. Example of testing combined measures in a shallow, urban pond (Eindhoven, the Netherlands). Biomanipulation (BM, fish stock reduction and introduction macrophytes) was not sufficient to change the water from turbid to clear, but combined with chemical P fixation in the sediment (using Phoslock®) or sediment nutrient removal (Dredging), the water became clear with abundant macrophytes and a good water quality was achieved (in the two consecutive years of the experiment; Waajen et al., 2016b). Chemical P inactivation reduced sediment P release, dredging exposed former agricultural soil (Waajen et al., 2016b).

Fig. 7. Hysteresis in a typical shallow lake in which increased nutrient loading leads to a shift from a clear water state with submerged macrophytes to a phytoplankton-dominated state, where the critical point of return is at lower loading than the transition to a turbid state (cf. Scheffer et al., 1993). Shifts indicated by dotted lines. Combined measures reducing turbidity and lowering nutrient load far enough (grey arrow) will bring a system in a clear water state. Above the critical loading, effects will be short-lived and the system will return to a turbid state (light grey arrow). (Redrawn from Lürling et al., 2016b).
epilimnion and transport them to the sediment. “Flock and Lock” strategies or only P-fixation can be powerful techniques to control internal P load. In many water bodies, a reapplication will be needed. This can be within one season, or every year in waters with ongoing external load (point source, diffuse or both) or even within several years to decades in waters with a relatively small diffuse load. All in all, geo-engineering techniques provide valuable possibilities in the tool-box of lake managers and water authorities to minimize the impact of cyanobacterial nuisance in lakes, ponds and reservoirs.

Declaration of Competing Interest

None.

Acknowledgements

Li Kang is sponsored by a CSC Grant (China). VLMH and MMM are partially supported by the National Council for Scientific and Technological Development (CNPq), Brazil. This review is part of the CAPES-ANA project (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES)/Agência Nacional de Águas (ANA), Brazil and CIANO-Control project (CNPq, Brazil) and was partly conducted under the flag of the CAPES (Brazil)/NUFFIC (The Netherlands) project 045/12.

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