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Editorial – a critical perspective on geo-engineering for eutrophication management in lakes

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Short Title: Geo-engineering to manage eutrophication in lakes

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Abstract

Eutrophication is the primary worldwide water quality issue. Reducing excessive external nutrient loading is the most straightforward action in mitigating eutrophication, but lakes, ponds and reservoirs often show little, if any, signs of recovery in the years following external load reduction. This is due to internal cycling of phosphorus (P). Geo-engineering, which we can here define as activities intervening with biogeochemical cycles to control eutrophication in inland waters, represents a promising approach, under appropriate conditions, to reduce P release from bed sediments and cyanobacteria accumulation in surface waters, thereby speeding up recovery. In this overview, we draw on evidence from this special issue *Geoengineering in Lakes*, and on supporting literature to provide a critical perspective on the approach. We demonstrate that many of the strong P sorbents in the literature will not be applicable in the field because of costs and other constraints. Aluminium and lanthanum modified compounds are among the most effective compounds for targeting P. Flocculants and ballast compounds can be used to sink cyanobacteria, in the short term. We emphasize that the first step in managing eutrophication is a *system analysis* that will reveal the main water and P flows and the biological structure of the waterbody. These site specific traits can be significant confounding factors dictating successful eutrophication management. Geo-engineering techniques, considered collectively, as part of a tool kit, may ensure successful management of eutrophication through a range of target effects. In addition, novel developments in modified zeolites offer simultaneous P and nitrogen control. To facilitate research and reduce the delay from concept to market a multi-national centre of excellence is required.

Key words: eutrophication management, geo-engineering in lakes, lake rehabilitation, system analysis, phosphorus sorbent

1. Introduction

Human activities have resulted in enrichment of surface waters with nutrients, mainly nitrogen (N) and phosphorus (P). This cultural eutrophication has become a worldwide water quality issue (Smith and Schindler, 2009) and is recognised by scientists as the most important water quality problem (Downing, 2014). One of the symptoms of eutrophication is excessive phytoplankton growth, mainly cyanobacteria, which may cause nuisance blooms (Carpenter et al., 1998). Such blooms have negative consequences for ecosystem functioning and ecosystem services. Cyanobacterial blooms can obstruct the use of lakes, ponds and reservoirs as sources of drinking water, agricultural irrigation, fishing, industry water and recreation (Carmichael, 2001; Codd et al., 2005; Smith and Schindler, 2009) resulting in severe economic costs (Steffensen, 2008; Dodds et al., 2009). Thus, controlling eutrophication and mitigating nuisance cyanobacteria is an essential task.

Reducing excessive external nutrient loading is in principal the first adaptive management measure (Cooke et al., 2005). External load reduction may cause desired changes in lakes, but often little, if any, signs of recovery are observed in the years following external load reduction (Jeppesen et al., 1991). The main process responsible for maintaining symptoms of eutrophication following catchment management is internal cycling of P. The in-lake P is released from a sediment pool which accumulated during the period of high external loading (Cooke et al., 2005). This internal P loading can delay lake recovery for decades (Søndergaard et al., 1999; Cooke et al., 2005; Fig. 1A) and it can, therefore, be necessary not only to reduce external P-loading, but also to mitigate the effects of internal P cycling from the sediment. Here, geo-engineering approaches, which are defined as the manipulation of biogeochemical processes (commonly targeting P) using materials to achieve a desired chemical and/or ecological response (Spears et al., 2014), represent a suite of tools with which water quality can be improved in the short term, thereby speeding up recovery (Fig. 1B).

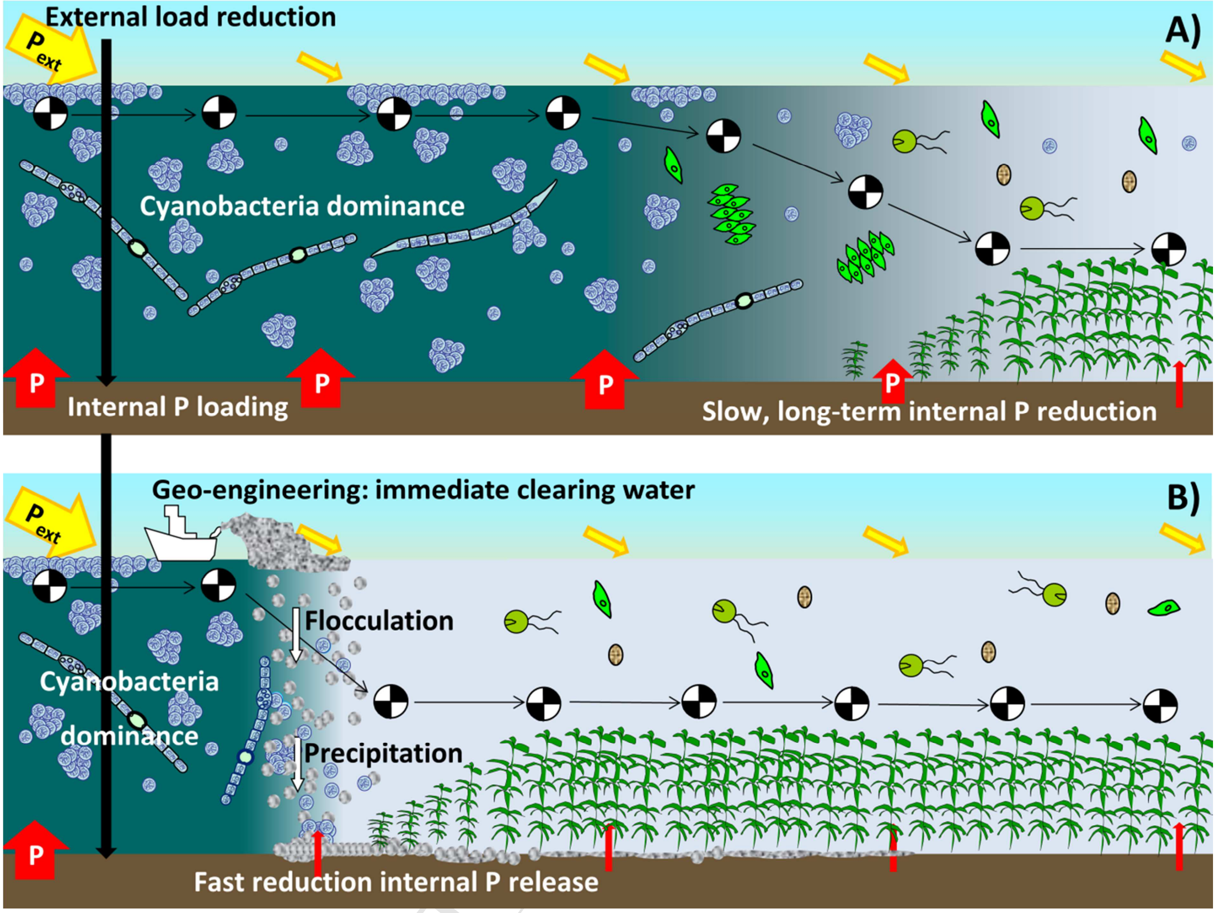

Figure 1: Eutrophic lake with a delayed recovery in water quality (diminishing toxic cyanobacteria blooms) after external P load reduction due to eutrophication stabilizing internally stored P (upper panel A) and geo-engineering speeding up recovery through precipitation of water column P and cyanobacteria and chemical P fixation in the sediment (Panel B).◐ *indicates the Secchi depth as a measure of water clarity.*

2. Chemical P inactivation

With increasing population growth and resulting environmental change, the abatement of P inevitably requires in-lake interventions. Reducing external P load to lakes will generally be insufficient to mitigate nuisance eutrophication symptoms, especially in the short term, as those actions are predominantly tackling manageable point sources only (Carpenter et al., 1998). Non-point sources from P saturated soils and ground water together with in-lake P cycling may limit recovery for decades to centuries (Carpenter 2005; Jarvie et al., 2013). Hence, in-lake geo-engineering tools to specifically counteract diffuse groundwater P inflow and to constrain internally stored P are attractive additional measures.

There is a wealth of literature on PO_4-P sorbents ranging from metal salts, minerals, clays, fabricated oxides, layered double hydroxides and modified clays to industrial waste products, amongst others (see Supplementary information Table S1). These products encompass a wide range of P adsorption capacities from less than 1 mg P g^{-1} sorbent to more than 100 mg P g^{-1} sorbent (Table S1). When comparing the P adsorption capacities of different products in view of lake restoration, several additional aspects should also be taken into consideration. For successful field application, the P-sorbent should not only possess an affinity to adsorb P and to retain its adsorption capacity under naturally occurring conditions, but it should also be safe, cheap and easy to prepare and use. These criteria render many seemingly promising P-sorbents virtually inapplicable. For instance, layered double hydroxides with high phosphate adsorption capacities (47 – 71 mg g^{-1}, Jiang and Ashekuzaman, 2014), porous $Pr(OH)_3$ nanowires (129 mg g^{-1}, Tang et al., 2014), binary oxides (35 mg g^{-1}, Li et al., 2014; 12 mg g^{-1}, Long et al., 2011), and ceramic biomaterials (14 mg g^{-1}, Chen et al., 2014) are too elaborate to manufacture and too expensive to be applied at the ecosystem scale. Other materials, such as red mud (114 mg g^{-1}, Li et al., 2006), may come with toxicity issues (Misík et al., 2014). Materials may also exhibit far less P adsorption under natural conditions than their theoretical maximum as determined in a laboratory setting, which further limits their usefulness. La-modified zeolite has reduced P-adsorption at pH slightly above 8, presumably through competition with hydroxyl ions (Ning et al., 2008), iron impregnated coir pith had high P-adsorption capacity (71 mg g^{-1}) at pH 3, but P-removal dropped to 20-30% at pH 8 (Krishnan and Haridas, 2008), while Al-pillared smectites expressed P-adsorption capacities of 20-27 mg g^{-1} at pH 3-4, but of only 5-7 mg g^{-1} at pH 6-7 (Kasama et al., 2004). Higher pH values are quite common in shallow eutrophic waterbodies, especially during periods of high primary productivity, and thus binding capacity at realistic pH values need to be better quantified.

Several studies have reported laboratory based comparisons of the PO_4-P adsorption maxima of tested materials with those of products in the literature, basing claims on material performance on unrealistic, or at times generally qualitative, comparisons (e.g., Zamparas et al., 2013; Lu et al., 2014; Tang et al., 2014; Xie et al., 2014; 2015). However, comparing results from different studies should be done with caution as different conditions can have pronounced effects on the reported P-adsorption values, and these effects may be site- and material-specific.

In general, Fe-based P-sorbents should only be considered for use under aerobic conditions (i.e. redox potential >200 mV), where Fe-modified sorbents act, most likely, through exchange of hydroxide (OH^-) with phosphate ($H_2PO_4^-$) (Cooke et al., 2005). In contrast, under anoxia (i.e. <200 mV) reduction of Fe–P complexes will result in release of phosphate. This also holds true for zero-valent-iron (ZVI) that may express extremely high P-sorption capacity (Table 1), but of which the anaerobic corrosion product is soluble Fe^{2+} (Su and Puls, 2003). Low redox conditions are common in the hypolimnion and near or in the sediments of eutrophic lakes and reservoirs (Boström et al., 1988). Al- or La-modified clays do not suffer from redox sensitivity and block sediment P release equally well under aerobic and anaerobic conditions (Gibbs et al., 2011). The La modified bentonite Phoslock expressed almost equally good P-adsorption under anoxic as under aerobic conditions (Noyma et al., this issue) and reduced sediment P release, accordingly (Ross et al., 2008; Gibbs et al., 2011).

Experiments should include efficacy as well as environmental safety studies performed under realistic conditions.

3. The need for comprehensive ecosystem scale diagnosis – an introduction for water managers

Too often in the literature has failure of in-lake management measures been linked to failure to reduce catchment nutrient load sufficiently. This suggests a breakdown in communication between research scientists and water managers and we propose a simple systems analysis approach to address this issue, below.

In the sequence from identification of a water quality problem to the desired improvement in specific ecosystem services water authorities mostly focus on problem identification and the implementation of measures (Fig. 2).

Figure 2: Sequence from identifying a water quality problem to the desired improved ecosystem services.

The problem (phytoplankton bloom) might be obvious and justify action even if stakeholders do not realize they are affected (e.g. suffering health risk). However, in problem solving, identification of the cause(s) is crucial in order to address the problem adequately. This is the purpose of the proposed system analysis (SAL). It is aimed to determine a water and P-balance of the waterbody, the drivers of movement of P, and the biological make-up of the system and its function(s) and thus is an essential aid in decision-making. The SAL determines the magnitude of internal versus external P loadings. As external P loading is often partly linked to water flows, the determination of a water balance is a requirement in quantifying the P input from water related sources (*see* chapter 3 in Cooke et al., 2005). In addition, a water balance gives insight into a water body's retention time. The water balance can be based on the general equation (Nõges , 2005):

$$I + Pr - E - O \pm \Delta V = 0$$

In which, I = Inflow (surface runoff, groundwater, surface water), Pr = Precipitation onto the water surface, E = Evaporation from the water surface, O = Outflow, ΔV = Change in storage during the period in question.

Part of the external P input, however, comes from sources that are not linked to water flows. The sources that can be particularly important in smaller lakes and ponds are feeding fish with bread (Turner and Ruhl, 2007), or boilies (Niesar et al., 2004), leaf litter falling from branches directly over the water (Delong and Brunsven, 1994) and water birds visiting the lakes and ponds (Hahn et al., 2008). Hence, quantification of the total P input implies the quantification of both the water related sources and the other sources. The P-load will be site specific and can be determined based on measurements and estimates from data (*see* Waajen et al., this issue-b, Appendix A for a more detailed description of various sources).

An estimate of the P flux from the sediment, as well as dose of materials to control it, can be measured in intact sediment cores brought into the laboratory (Hansen et al. 2003; Meis et al., 2013). The overall P-loading for shallow lakes can be evaluated by using the model PCLake (Janse et al., 2008) that will indicate the critical P-loads for clear to turbid water and vice versa for the specific water bodies (Fig. 3). Of particular importance for shallow lakes is an assessment of the fish stock. High biomass of benthivorous fish (carps and breams) can easily keep the water in a turbid state by resuspending sediments and preventing submerged macrophyte establishment (e.g., Cline et al., 1994; Roozen et al., 2007). Abundant sediment resuspending fish can also undermine the efficacy of the in-lake interventions

(Huser et al., this issue-b). Therefore, biomanipulation should be considered an essential structural measure to be implemented for rehabilitation of such waters (Gulati and Van Donk, 2002; Van Donk et al., 1994).

For deep lakes, proxies to derive acceptable P loadings can be used (e.g. Vollenweider, 1976). Two contributions in this special issue estimated critical P-loads for three water bodies (Waajen et al., this issue-a,b).

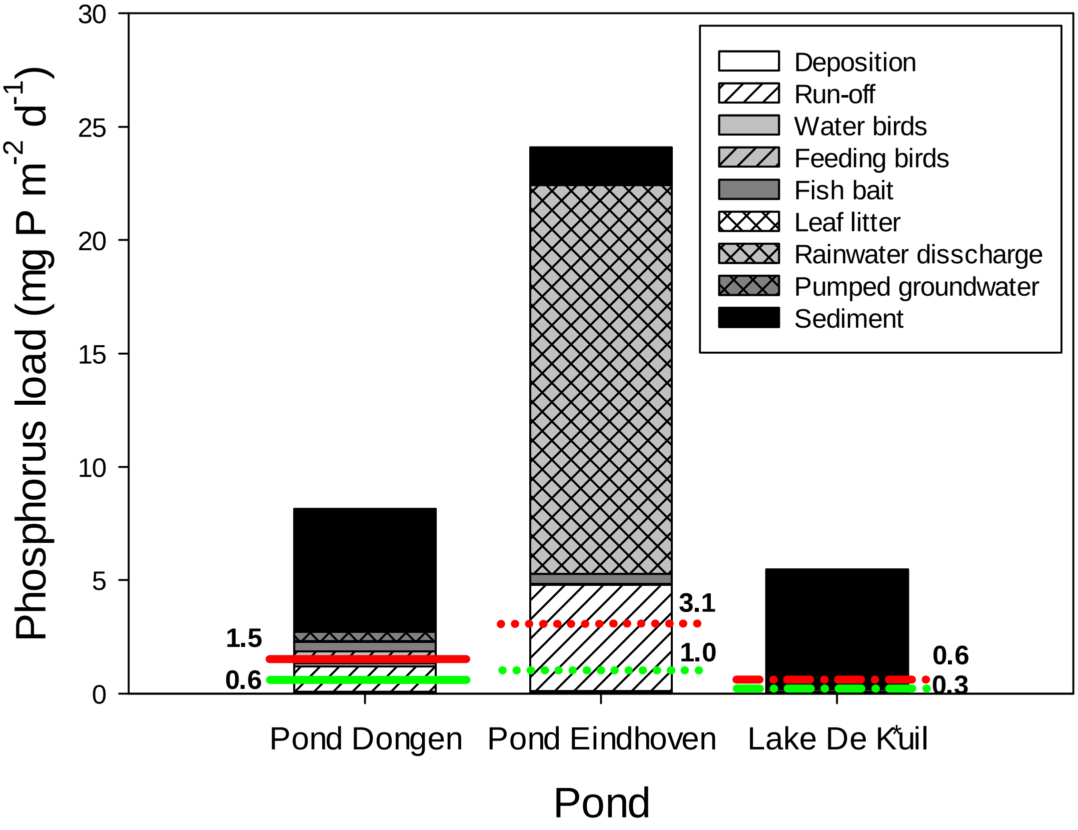

Figure 3: Estimated phosphorus loadings of several sources to Pond Dongen, Pond Eindhoven and Lake De Kuil, including the critical loading for the transition from a clear water to a turbid water (red lines) and for the transition from a turbid water to a clear water (green lines) as determined using PCLake for the ponds and Vollenweider (1976) for the lake.

Despite the fact that the uncertainty in these estimates is likely to be around a factor of two (Janse et al., 2010) and the magnitude of the various P-loads will contain errors, they indicate the general level of P load reduction required and provide insight into which sources need to be tackled to achieve the highest chance for success. Thus, a SAL is useful for underpinning the prioritisation of lake management strategies. For example, in the three water bodies shown in Figure 3, the estimated P loading was considerably larger than the critical loadings and following Janse et al. (2008) the primary option for rehabilitation would be to decrease catchment P loads. The SAL pointed to different solutions for each of these waters. In Lake De Kuil, the internal loading (~5.2 mg P m^{-2} d^{-1}) made up about 95% of the total P-load (~5.5 mg P m^{-2} d^{-1}) and thus strongly reducing the internal load could bring the total remaining load in the estimated range for clear water (~0.3 – 0.6 mg P m^{-2} d^{-1}; Fig. 3). In Pond Dongen, where the internal P-load (~5.4 mg P m^{-2} d^{-1}) contributed 67% to the total estimated P-loading (~8.1 mg P m^{-2} d^{-1}), solely tackling internal P-loading would not be sufficient to bring the water to a clear state (critical loadings 0.6 and 1.5 mg P m^{-2} d^{-1}). Consequently, additional measures targeting external sources would be needed. Likewise, in Pond Eindhoven strong reduction of external inputs would be needed (Waajen et al., this issue-b); the internal P load only contributed 7% to the total estimated P-loading and external inputs through run-off and rainwater discharge were dominant such that without the large reduction of these P inputs, all other measures would be futile (Fig. 3). Accordingly, the consequence of a SAL is that tailor-made solutions will result, and most probably a set of measures rather than one single measure will be proposed.

Lake managers, however, also need to consider other aspects such as safety and costs. The cost of maintenance management and essential effects monitoring should be assessed against the cost of doing nothing (Mackay et al., 2014). Hence, only after a SAL which preferably includes a societal cost-benefit analysis, the most promising measures can be selected (Fig. 4). In this special issue, a one-box model is proposed, which is a mass balance tool for predicting the P trend in the water under different management options that was applied to the deep Lake Arendsee (Hupfer et al., this issue). By running different scenarios, the authors could identify the magnitude of effects of external load reduction combined with in-lake P inactivation as single or repeated applications (Hupfer et al., this issue). This approach illustrates the power of a thorough SAL and an evaluation tool for testing the expected longevity and impact of mitigation alternatives. Together with a cost-benefit analysis the most promising set of measures can be chosen (Fig. 4).

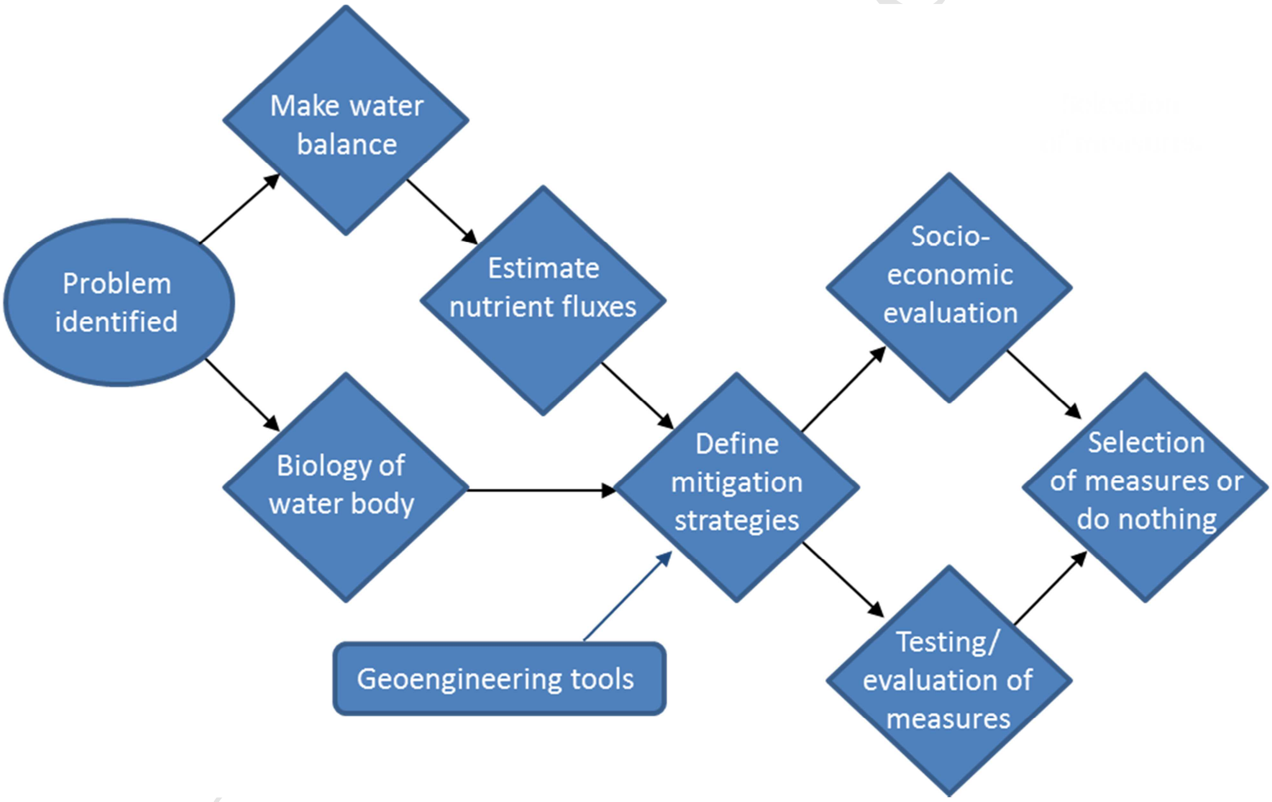

Figure 4: Once a eutrophication problem has been identified in a lake, a system analysis, which includes determination of water- and nutrient balances, the biological composition of the lake, socio-economic analysis on costs and benefits, and an evaluation of performance and longevity of the proposed measures, will underpin the selection of measures that may include geoengineering tools or leave 'do nothing' as an option.

4. Chemical P inactivation as a geo-engineering tool in the field

The selected studies listed in Table S1 provide a whole array of interesting compounds, but information on efficacy under realistic conditions, i.e. using lake water (e.g. Ross et al., 2008; Reitzel et al., 2013) or low redox are missing in most cases. In addition, studies on potential side-effects and *in situ* trials are generally lacking. In contrast, iron-, calcium- and aluminium salts, and the lanthanum modified bentonite Phoslock® have been used from one to several decades in lake rehabilitation of which both Al and La have been most widely applied (Huser et al., this issue-a,b; Copetti et al., this issue). It is, therefore, not surprising that the majority of contributions to this special issue focussed on these compounds as important components in geo-engineering, and these are reviewed below.

Aluminium

Two manuscripts in this special issue focussed on Al in controlling eutrophication. The first study (Huser et al., this issue-a) described the restoration of the Minneapolis Chain of lakes in Minnesota (USA). External load reduction was inadequate to maintain good water quality in these urban lakes and in-lake alum dosing yielded variable results. Huser et al. (this issue-a) ascribed the variation in long-term effectiveness of whole-lake alum treatments to a poor understanding of the P loads to the lakes and inaccurate calculation methods for alum doses. In particular, the alum dose should be determined based on the amount of mobile P in the sediment – preferably in the upper 10 cm of the sediment (Reitzel et al., 2005; Huser et al., this issue-b). A thorough review of 114 alum treated lakes demonstrated clearly that treatment longevity in deeper, stratified lakes was longer (mean 21 years) than in shallow, polymictic lakes (mean 5.7 years) where, for amongst other reasons, sediment disturbance by bottom feeding fishes (carp) reduced longevity of the treatment (Huser et al., this issue-b). Moderate densities of carp can increase the sediment mixed layer from 5 cm without carp to 16 cm with carp and thus proliferate the amount of mobile sediment P that might be released to the water column (Huser et al., 2015). Huser et al. (this issue-b) also concluded that adequate monitoring programs are needed to yield more insight into factors affecting longevity of Al additions to lake sediments to further improve the effectiveness of future treatments.

Use of polyaluminium chloride as a flocculent (Noyma et al., this issue; Waajen et al., this issue-b) has been demonstrated to effectively aggregate cyanobacteria and sink them with a ballast out of the water column.

Iron

Compared to Al, less field trials with Fe to inactivate P have been reported. In general, the redox sensitivity of Fe is viewed as a major drawback of using Fe in counteracting eutrophication in lakes (Cooke et al., 2005). Oxygen consumption due to bacterial breakdown of organic matter is a key process in the reduction of Fe and sulphate which may cause a strong decrease in the P-binding capacity of sediments due to the formation of FeS_x (Smolders et al., 2006). Recently however, Immers et al. (2015) reported promising results of $FeCl_3$ addition (33 g Fe m^{-2}) to a lake over 1.5 years, with lower P and cyanobacteria biomass, but they also indicated sulphate and DOC as confounding factors to the success of the treatment. Under aerobic conditions Fe may effectively trap P (Smolders et al., 2006). A recent study reported gradual long-term (20 years) improvements in water quality following a single bulk Fe addition, despite annual anoxic events, which diminished as a consequence of less organic matter accumulation (Kleeberg et al., 2013). Nonetheless, the slowness and dependence of such gradual organic matter decrease will not always meet the ambitions of water authorities for rapid results. Novel developments include Fe-modified clays, such as Bephos™ (Zamparas et al., 2013) and Sinobent® (Goldyn et al., 2014). The latter is an iron, magnesium, calcium and nitrate modified bentonite, which showed promising results in an enclosure study (Goldyn et al., 2014). The addition of nitrate could increase the redox potential in the sediment and, thus, lower the internal loading of P from bottom sediments.

The contribution of Waajen et al. (this issue-a) included iron(III) chloride as a flocculent to aid rapid settling of a developing *Aphanizomenon flos-aquae* bloom from the water column to the bed sediments.

Calcium

When photosynthesis drives pH to values above pH 9.0 - 9.5 calcite will precipitate with possible co-precipitation of P (House, 1990; Danen-Louwerse et al., 1995; Cooke et al., 2005). The formed P precipitates, such as hydroxyapatite, but also calcite, have low solubility at pH higher than 9 (Cooke et al., 2005) and consequently, application of Ca to manage P is primarily suited for hard water lakes with relatively high pH, where liming could lower sediment P release substantially (Prepas et al., 2001; Zhang et al., 2001). Laboratory experiments with sediment from eutrophic German lakes showed that active calcite barriers could strongly reduce the P efflux from the sediment (Berg et al., 2004). Several calcite characteristics like grain size, specific surface and structure determine the P adsorbing capacity (Berg et al., 2004), while complexation can be hindered by organic matter and iron-ions (Dittrich et al., 2011). A combined sodium aluminate and Ca hydroxide treatment applied to the hypolimnion strongly reduced the P diffusion rates from the sediment of Tiefwarensee and caused a rapid trophic shift that lasted at least for 7 years (Wauer et al., 2009). The latter study emphasized the importance of a P balance and applied a one-box model to predict the long term outcome of the rehabilitation (Wauer et al., 2009).

Lanthanum modified clay (LMB)

This special issue comprises numerous contributions related to the CSIRO developed lanthanum modified bentonite Phoslock® (LMB) (Douglas, 2002) that was brought to the market about a decade ago.

A re-evaluation of one of the first in-situ applications of LMB in the Canning River, Western Australia, with special focus on the interpretation of nutrient ratios and concentrations, demonstrated that LMB can result in a rapid and effective removal of soluble reactive P (SRP) from the water column and intercept and capture SRP released from bottom sediments (Douglas et al., this issue). Consequently, LMB caused a shift from potential N-limitation to potential P-limitation as was predicted by nutrient limitation diagrams (Douglas et al., this issue). Development, experiments from lab to field scale, applications and safety are evaluated in a comprehensive review of LMB (Copetti et al., this issue). The results unambiguously showed effective reduction of SRP concentrations in the water column and of sediment SRP release, under most environmental conditions, and across laboratory, mesocosm and field scales in freshwater ecosystems. The response of phytoplankton is less well characterised, but in a study of LMB application to Loch Flemington, UK, initial declines in phytoplankton biomass following the LMB application were accompanied by algal community shifts which resulted in a reduction in the dominance of cyanobacteria relative to other species and a more functionally diverse algal community (Lang et al., this issue). Likewise, a recent study from Canada reported cyanobacteria blooming before LMB treatment, but not after (Nürnberg and LaZerte, 2016).

A detailed evaluation of LMB treated lakes found reductions in surface water TP (data available from n = 15 lakes), SRP (n = 14 lakes) and chlorophyll *a* concentrations (n = 15 lakes) with increased Secchi disk depth (n = 15 lakes) (Spears et al., this issue). In addition, increases in aquatic macrophyte community species numbers (average increase of 1.6 species; n = 6 lakes) and maximum colonisation depths (mean increase of 0.7 m; n = 4 lakes) were reported (Spears et al., this issue). The median values of TP, SRP and chlorophyll *a* concentrations across the lakes in the 24 months following LMB application were correlated positively with pre-application DOC concentrations, suggesting DOC as a factor potentially confounding the operational performance of LMB (Spears et al., this issue). Indeed, on a short-term scale the efficacy of LMB is reduced in the presence of humic substances (Lürling et al., 2014; Dithmer et al., this issue –a). It is also likely that other oxyanions can compete with phosphate for LMB (Reitzel et al. 2013; Copetti et al., this issue). Over time the confounding effects of humic substances seem to diminish and hence LMB will slowly reach its theoretical binding capacity (Dithmer et al., this issue –a). In LMB treatments La-P mainly precipitates as rhabdophane, which was confirmed in a laboratory experiment as well as a survey of sediments from 10 LMB treated lakes in Europe (Dithmer et al., 2015; Dithmer et al., this issue –b). About 25% of the sequestered SRP was identified as surface-P adsorbed to the surface of rhabdophane, but the strength of the resultant complex remains to be determined. The sequestered P is slowly transformed from the immediately formed rhabdophane towards monazite (Dithmer et al., this issue –a). Thus, there is very strong evidence for permanent removal of P by LMB from the water and sediment P pool.

As LMB primarily targets the mobile P pool in the sediment, sediment La content increased substantially after LMB treatments (Yasseri and Epe, this issue). The determination of the La:P ratio in different sediment depth strata provided a good insight into dose-sufficiency (Yasseri and Epe, this issue). The suspended solids concentration and filterable La concentration were also elevated just after LMB applications and in general declined in the months following application (Spears et al., 2013). No clear ecotoxicological issues with the use of LMB have been identified to date, yet use of LMB in soft waters, saline waters and waters with low pH is not recommended due to potential risk of elevated concentrations of trivalent La ions in the water column (Copetti et al., this issue).

5. Stripping cyanobacteria from the water column

In situations where it is not economically or technically feasible to reduce external P-loading, effect oriented or curative measures may provide the most suitable nuisance control. The most straightforward curative measure to remove nuisance cyanobacteria from the water is by using algaecides that kill the cyanobacteria, yet such interventions are probably very short lived and can immediately liberate nutrients and toxins to the water column or have other constraints (Janĉula and Maršálek, 2011). An alternative might be harvesting cyanobacteria from the water, but these actions come with high costs and generally with limited effectiveness in larger water bodies.

Flocculants and ballast

Flocculation and sedimentation with clay might be a cost-effective approach for controlling marine harmful algal blooms (Anderson, 1997; Sengco and Anderson, 2004). Adding a flocculent, such as polyaluminiumchloride (PAC), lowered the dose of clay needed and also improved the removal of red tide species (Sengco and Anderson, 2004; Hagström and Granéli, 2005). In fresh waters the low ionic strength of the water impairs clay flocculation of cyanobacteria (Han and Kim, 2001; Pan et al., 2006a). However, this drawback can be overcome by modifying the clay with a flocculent; addition of Fe^{3+}, polyacrylamide or chitosan improved flocculation and removed > 90% of cyanobacteria (Pan et al., 2006b; Zou et al., 2006). Use of local sands or clays as ballast may reduce transport costs. Combined flocculent (10 mg L^{-1} chitosan plus 10 mg L^{-1} PAC) and a local sand (100 mg L^{-1}) showed good removal in a laboratory experiment (Pan et al., 2011a). Likewise, Shi et al. (this issue) used cationic starch as flocculent (10 mg L^{-1}) that combined with a local soil (100 mg L^{-1}) stripped experimental jars clear of cyanobacteria, although not necessarily to below safe levels for human health as indicated by the World Health Organisatoin (i.e. < 20,000 cells ml^{-1}). Yuan et al. (this issue) used chitosan-acidic coal fly ash leachate and coal fly ash (100 mg L^{-1}) to flock and sink *Microcystis aeruginosa* out of the water column. Noyma et al. (this issue) showed that flocculation with either PAC or chitosan (2 mg L^{-1}) and local red soil as ballast (160-320 mg L^{-1}) effectively precipitated buoyant cyanobacteria harvested from a reservoir. In another laboratory experiment, Li and Pan (2015) successfully settled cyanobacteria from water using chitosan-modified local soil (2 mg L^{-1} chitosan and 100 mg L^{-1} soil) and demonstrated reduced microcystin concentrations. Applying the flocculent-modified soil technique in the field, at 40-50 g m^{-2} (~25-31 mg L^{-1}), Pan et al (2011b) demonstrated the clearance of cyanobacteria from surface waters within an isolated bay (Pan et al., 2011b). The dual mechanism of surface charge and netting-bridging modification when soil or clay is modified using flocculants, yields high removal rates of cyanobacteria in both freshwater and marine environments (Li and Pan, 2013).

Wang et al. (this issue) developed an integrated biotic toxicity index (BTI) to assess the toxicity potential of chitosan, cationic starch, chitosan modified soil and cationic starch modified soil to several aquatic organisms. They found acute toxic effects for both flocculants on algae, *Daphnia*, tubifex and fish at doses commonly used (0.9 – 6.9 mg L^{-1}), and although adding soil elevated these values considerably (90 – 323 mg L^{-1}) these results highlight the need for more research on possible chronic eco-toxicological effects associated with this approach (Wang et al., this issue).

In future it is important that the effects of methods for the removal of cyanobacteria from surface waters, similar to those outlined above, be quantified against public health targets including cyanotoxin and cyanobacteria abundance.

Flocculants and solid-phase P fixative as ballast

The combination of a flocculent and a solid phase P-sorbent can be used. P stored in cyanobacteria cells in the water column can reach hundreds of μg L^{-1} at times when water column SRP will be below the level of detection. A solid phase P-sorbent can neither bind particulate P, nor precipitate the cyanobacteria out of the water column (Lürling and Van Oosterhout, 2013), resulting in little to no effect on the P present in the water column during a bloom. This biological P component might be a sufficient P reservoir to maintain high risk for ongoing cyanobacterial blooms following flocculation to the bed sediments. So, the combination of flocculent plus solid phase P-sorbent strips the water column of cyanobacteria, sinks them to the sediment, and blocks internal P loading (Lürling and Van Oosterhout, 2013). This technique has been demonstrated at the field scale in Lake Rauwbraken (Van Oosterhout and Lürling, 2011; Lürling and Van Oosterhout, 2013) and Lake De Kuil (Waajen et al., this issue-a), two isolated and stratifying lakes in The Netherlands. In Lake Rauwbraken PAC was used as a flocculent whereas iron (III) chloride was used in Lake De Kuil. In both lakes LMB was used as ballast and solid-phase P sorbent. Flocculants combined with solid-phase P fixative as ballast is also advisable for lakes and ponds with perennial blooms; otherwise a solid phase P sorbent may suffice (Waajen et al., this issue-b).

An initial disappearance of *Daphnia* from Lake Rauwbraken was attributed to physical effects of flocks, grazing inhibition of flocks and clay, very low food concentrations, and the absence of predation refugia, but these effects were temporary and *Daphnia* recovered within several months of the treatment (Van Oosterhout and Lürling, 2011).

6. Geo-engineering in managing eutrophication

Whilst it is beyond doubt that in-lake activities counteracting sediment P release, can be effective in controlling cyanobacteria blooms for many years in cases where external nutrient load is not (or no longer) a main issue (e.g., Lürling and van Oosterhout, 2013;

Waajen et al., this issue-a), there might be other reasons that warrant research on mitigating in-lake N. For instance, high inorganic N concentrations may come with toxicity issues to various aquatic organisms (Camargo et al., 2005; Camargo and Alonso, 2006), it may lead to more disease in water clearing zooplankton (Dallas and Drake, 2014) and may have negative effects on clear water stabilising macrophytes (Olsen et al., 2015). In spite of the fact that nitrate and ammonium salts are soluble and atmospheric nitrogen inputs can pose serious problems for lakes, in-lake N might be reduced partly through ammonium adsorption by zeolites (e.g., Klieve and Semmens, 1980; Wen et al., 2006). Zeolites are natural porous minerals -crystalline hydrated aluminosilicates- and strong cation absorbers (Wen et al., 2006). Zeolites can concomitantly reduce the P and ammonium efflux from sediment (Lin et al., 2011). Particularly, Al modified zeolite such as Aqual-P or Z2G1 actively remove both P and ammonium released from sediments (Gibbs et al., 2011), which makes it a very promising material for managing in-lake nutrient loads. More up-scaled research is needed as concurrently lowered in-lake N and P concentrations could also promote buffering against return to a more eutrophic state. Hence, there is a great potential for geo-engineering in controlling nuisance cyanobacteria and mitigating eutrophication.

Geo-engineering techniques will not be limited to in-lake measures. For instance, where bank erosion is a considerable source of P (Kronvang et al., 2012), bank enforcements and P-stripping agents can be implemented in the buffer zones. Sand filters incorporating lime combined with buffer zones were effective in reducing the P load to watercourses (Kirkkala et al., 2012). Likewise, P-stripping materials as iron-oxide based CFH-12 may be applied to intercept P at the end of agricultural drainage pipes (Lyngsie et al., 2014). The resulting external P load reductions are crucial in determining longevity of the in-lake measures (Hupfer et al., this issue). For instance, scenario analyses of Lake Arendsee (Germany) revealed that a gradual external P load reduction assured the sustainability of a planned Al application beyond one decade (Hupfer et al., this issue). When external P-load reductions are economically or technically difficult, curative measures should be an option.

It should be emphasized again that each mitigation should start with a SAL simply to avoid implementation of costly and ineffective measures. In addition, SAL driven eutrophication management should include thorough multi-year pre- and post-application monitoring. Only through such monitoring can an accurate assessment of the targets be carried out and a better understanding of the treatment efficacy and occurrence of unforeseen positive or negative side effects be gained; experience is the best teacher. Post-treatment monitoring can also reveal if the initial P fluxes were accurate and identify whether and when a follow up intervention may be required. Repeated interventions are not a favourite subject for water managers, but in many cases in urbanised areas with ongoing diffuse P-loads it is unlikely that one intervention will represent a permanent solution. In fact, Meis et al. (2013) proposed repeated applications of smaller doses of material to ensure effective dose is achieved most efficiently, although this represents a significant change from the typical ‘single dose’ approach. Particularly for official bathing sites or drinking water reservoirs regular maintenance should be a common aspect of authorities’ plans to keep the waters at such a quality that it can fulfil the services needed and deliver the goods demanded.

Most engineered solid phase P-sorbents, particularly the ones addressed in this special issue, are primarily designed to target internally released phosphate from lake bed sediments. As the contributions to this special issue demonstrate, geo-engineering in lakes by use of such P-adsorptive materials or flocculants and ballast can be a powerful approach to mitigate eutrophication. Eutrophication is recognised as the most important water quality issue worldwide (Smith and Schindler, 2009; Downing, 2014), yet, eutrophication research is not listed among the top three research paradigms studied by limnology (Downing, 2014). Instead of focussing on quick fix approaches, the diversity of surface waters demand a SAL guided approach to recognise the individual characteristics of each lake (Björk, 1972). Even though the use of P-adsorptive materials is a commonly used ‘geoengineering’ approach (Mackay et al. 2014), a multi-national collaboration and research centre to develop and test P and/or N adsorptive materials, flocculants and ballast compounds is strongly recommended to boost scientific insights and support the development and validation of emerging and novel compounds, reducing time from concept to market. New geo-engineering compounds should be effective, safe, cheap and easy to prepare and use, and an independent research and policy body is necessary to underpin this. The first step will be demonstrating efficacy and safety under controlled conditions (Fig. 5), moving to replicated field and ecosystem scale experiments (Fig. 5).

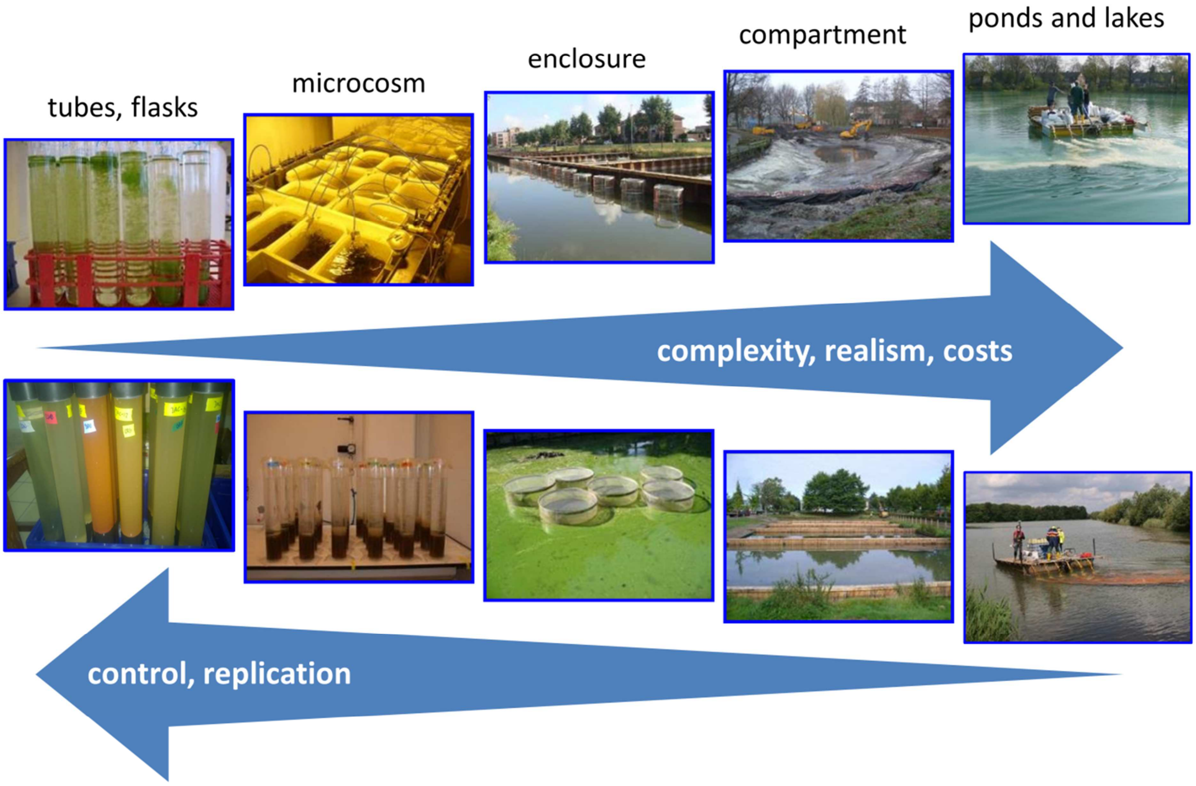

Figure 5: Research at various scales from controlled and replicated laboratorial experiments to whole lake experiments yielding a powerful balance between statistical power and reality .

7. Conclusions

- Geoengineering materials have been used to control phosphorus and cyanobacteria in lakes for decades.
- Numerous materials have been proposed or developed as strong P sorbents including metal salts, minerals, clays, fabricated oxides, layered double hydroxides and modified clays to industrial waste products. However, many are virtually inapplicable in situ due to high costs or other constraints.
- LMB and Al products have been most commonly applied as a result of their effective operational performance across a range of environmental conditions.
- Combining flocculants and ballast compounds (either P fixatives or just local soils) can be an efficient approach for the removal of particulate P (e.g. within cyanobacteria cells) from water-column to bed sediments.
- A system analysis to diagnose the main P and water flows as well as relationships with the biological composition of a water system should precede and guide management measures.
- Geo-engineering approaches provide powerful supplements to existing catchment management and biomanipulation measures for eutrophication management.

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