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**Editorial – A critical perspective on geo-engineering for eutrophication management in lakes.**

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

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21 *Short Title:* Geo-engineering to manage eutrophication in lakes

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26 **Abstract**

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

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

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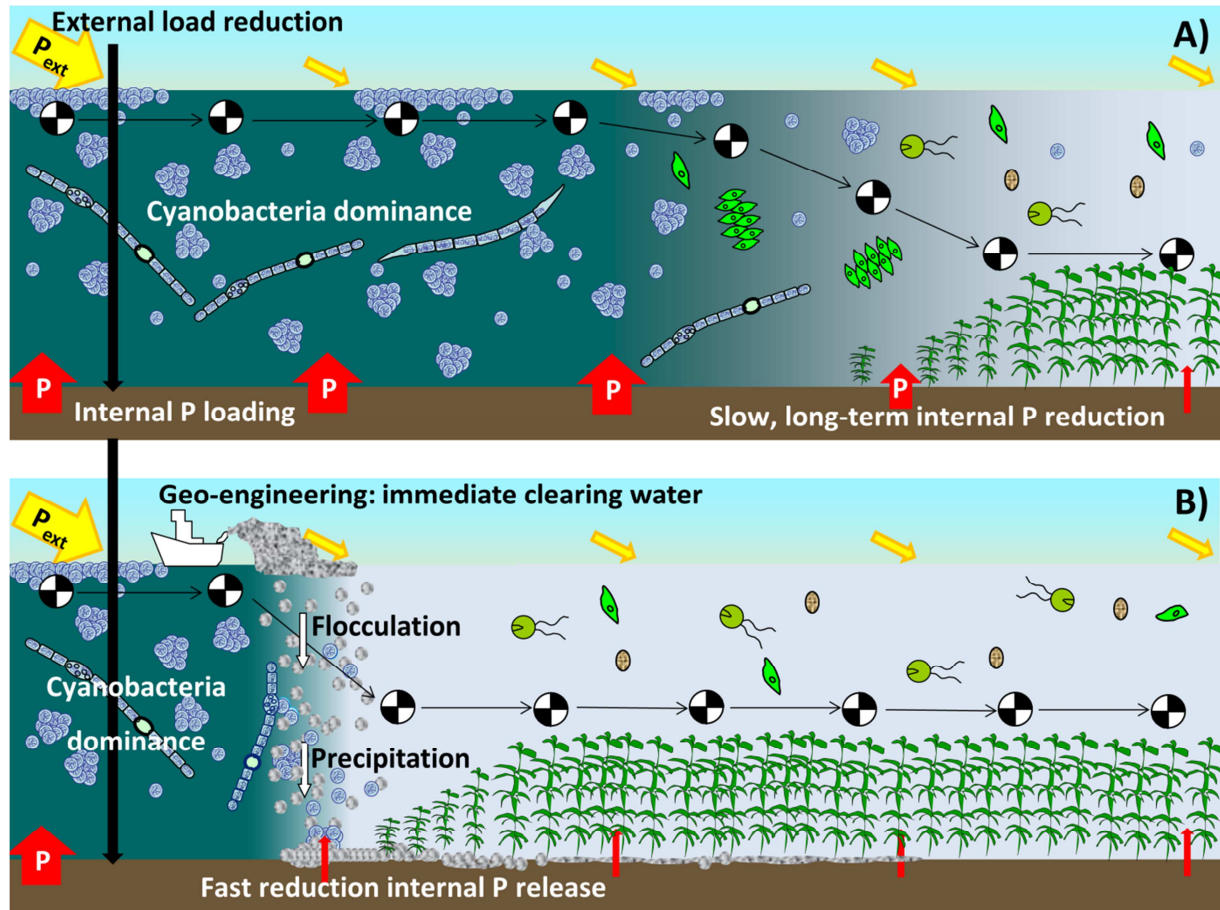
52 **1. Introduction**

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

64 Reducing excessive external nutrient loading is in principal the first adaptive  
65 management measure (Cooke et al., 2005). External load reduction may cause desired  
66 changes in lakes, but often little, if any, signs of recovery are observed in the years following  
67 external load reduction (Jeppesen et al., 1991). The main process responsible for maintaining  
68 symptoms of eutrophication following catchment management is internal cycling of P. The in-  
69 lake P is released from a sediment pool which accumulated during the period of high external  
70 loading (Cooke et al., 2005). This internal P loading can delay lake recovery for decades  
71 (Søndergaard et al., 1999; Cooke et al., 2005; Fig. 1A) and it can, therefore, be necessary not  
72 only to reduce external P-loading, but also to mitigate the effects of internal P cycling from  
73 the sediment. Here, geo-engineering approaches, which are defined as the manipulation of  
74 biogeochemical processes (commonly targeting P) using materials to achieve a desired

75 chemical and/or ecological response (Spears et al., 2014), represent a suite of tools with which  
 76 water quality can be improved in the short term, thereby speeding up recovery (Fig. 1B).

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*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).  $\odot$  indicates the Secchi depth as a measure of water clarity.*

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## 87 2. Chemical P inactivation

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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

90 insufficient to mitigate nuisance eutrophication symptoms, especially in the short term, as  
91 those actions are predominantly tackling manageable point sources only (Carpenter et al.,  
92 1998). Non-point sources from P saturated soils and ground water together with in-lake P  
93 cycling may limit recovery for decades to centuries (Carpenter 2005; Jarvie et al., 2013).  
94 Hence, in-lake geo-engineering tools to specifically counteract diffuse groundwater P inflow  
95 and to constrain internally stored P are attractive additional measures.

96         There is a wealth of literature on PO<sub>4</sub>-P sorbents ranging from metal salts, minerals,  
97 clays, fabricated oxides, layered double hydroxides and modified clays to industrial waste  
98 products, amongst others (see Supplementary information Table S1). These products  
99 encompass a wide range of P adsorption capacities from less than 1 mg P g<sup>-1</sup> sorbent to more  
100 than 100 mg P g<sup>-1</sup> sorbent (Table S1). When comparing the P adsorption capacities of  
101 different products in view of lake restoration, several additional aspects should also be taken  
102 into consideration. For successful field application, the P-sorbent should not only possess an  
103 affinity to adsorb P and to retain its adsorption capacity under naturally occurring conditions,  
104 but it should also be safe, cheap and easy to prepare and use. These criteria render many  
105 seemingly promising P-sorbents virtually inapplicable. For instance, layered double  
106 hydroxides with high phosphate adsorption capacities (47 – 71 mg g<sup>-1</sup>, Jiang and  
107 Ashekuzaman, 2014), porous Pr(OH)<sub>3</sub> nanowires (129 mg g<sup>-1</sup>, Tang et al., 2014), binary  
108 oxides (35 mg g<sup>-1</sup>, Li et al., 2014; 12 mg g<sup>-1</sup>, Long et al., 2011), and ceramic biomaterials (14  
109 mg g<sup>-1</sup>, Chen et al., 2014) are too elaborate to manufacture and too expensive to be applied at  
110 the ecosystem scale. Other materials, such as red mud (114 mg g<sup>-1</sup>, Li et al., 2006), may come  
111 with toxicity issues (Misík et al., 2014). Materials may also exhibit far less P adsorption under  
112 natural conditions than their theoretical maximum as determined in a laboratory setting, which  
113 further limits their usefulness. La-modified zeolite has reduced P-adsorption at pH slightly  
114 above 8, presumably through competition with hydroxyl ions (Ning et al., 2008), iron

115 impregnated coir pith had high P-adsorption capacity ( $71 \text{ mg g}^{-1}$ ) at pH 3, but P-removal  
116 dropped to 20-30% at pH 8 (Krishnan and Haridas, 2008), while Al-pillared smectites  
117 expressed P-adsorption capacities of  $20\text{-}27 \text{ mg g}^{-1}$  at pH 3-4, but of only  $5\text{-}7 \text{ mg g}^{-1}$  at pH 6-7  
118 (Kasama et al., 2004). Higher pH values are quite common in shallow eutrophic waterbodies,  
119 especially during periods of high primary productivity, and thus binding capacity at realistic  
120 pH values need to be better quantified.

121 Several studies have reported laboratory based comparisons of the  $\text{PO}_4\text{-P}$  adsorption  
122 maxima of tested materials with those of products in the literature, basing claims on material  
123 performance on unrealistic, or at times generally qualitative, comparisons (e.g., Zamparas et  
124 al., 2013; Lu et al., 2014; Tang et al., 2014; Xie et al., 2014; 2015). However, comparing  
125 results from different studies should be done with caution as different conditions can have  
126 pronounced effects on the reported P-adsorption values, and these effects may be site- and  
127 material-specific.

128 In general, Fe-based P-sorbents should only be considered for use under aerobic  
129 conditions (i.e. redox potential  $>200 \text{ mV}$ ), where Fe-modified sorbents act, most likely,  
130 through exchange of hydroxide ( $\text{OH}^-$ ) with phosphate ( $\text{H}_2\text{PO}_4^-$ ) (Cooke et al., 2005). In  
131 contrast, under anoxia (i.e.  $<200 \text{ mV}$ ) reduction of Fe-P complexes will result in release of  
132 phosphate. This also holds true for zero-valent-iron (ZVI) that may express extremely high P-  
133 sorption capacity (Table 1), but of which the anaerobic corrosion product is soluble  $\text{Fe}^{2+}$  (Su  
134 and Puls, 2003). Low redox conditions are common in the hypolimnion and near or in the  
135 sediments of eutrophic lakes and reservoirs (Boström et al., 1988). Al- or La-modified clays  
136 do not suffer from redox sensitivity and block sediment P release equally well under aerobic  
137 and anaerobic conditions (Gibbs et al., 2011). The La modified bentonite Phoslock expressed  
138 almost equally good P-adsorption under anoxic as under aerobic conditions (Noyma et al., this  
139 issue) and reduced sediment P release, accordingly (Ross et al., 2008; Gibbs et al., 2011).

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

142

### 143 **3. The need for comprehensive ecosystem scale diagnosis – an introduction** 144 **for water managers**

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

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



152

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

155

156 The problem (phytoplankton bloom) might be obvious and justify action even if stakeholders  
157 do not realize they are affected (e.g. suffering health risk). However, in problem solving,  
158 identification of the cause(s) is crucial in order to address the problem adequately. This is the  
159 purpose of the proposed system analysis (SAL). It is aimed to determine a water and P-  
160 balance of the waterbody, the drivers of movement of P, and the biological make-up of the  
161 system and its function(s) and thus is an essential aid in decision-making. The SAL  
162 determines the magnitude of internal versus external P loadings. As external P loading is often



163 partly linked to water flows, the determination of a water balance is a requirement in  
164 quantifying the P input from water related sources (*see* chapter 3 in Cooke et al., 2005). In  
165 addition, a water balance gives insight into a water body's retention time. The water balance  
166 can be based on the general equation (Nöges , 2005):

$$167 \quad I + Pr - E - O \pm \Delta V = 0$$

168 In which, I = Inflow (surface runoff, groundwater, surface water), Pr = Precipitation onto the  
169 water surface, E = Evaporation from the water surface, O = Outflow,  $\Delta V$  = Change in storage  
170 during the period in question.

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

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

188 (Huser et al., this issue-b). Therefore, biomanipulation should be considered an essential  
 189 structural measure to be implemented for rehabilitation of such waters (Gulati and Van Donk,  
 190 2002; Van Donk et al., 1994).

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

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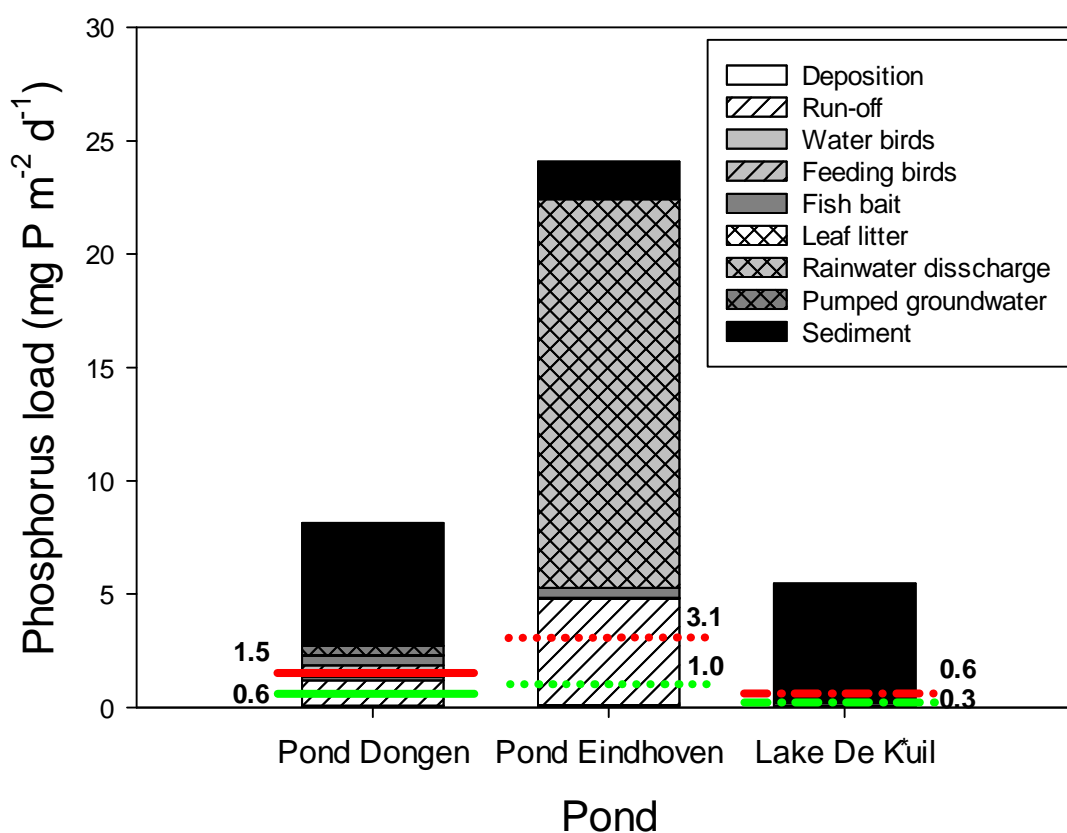
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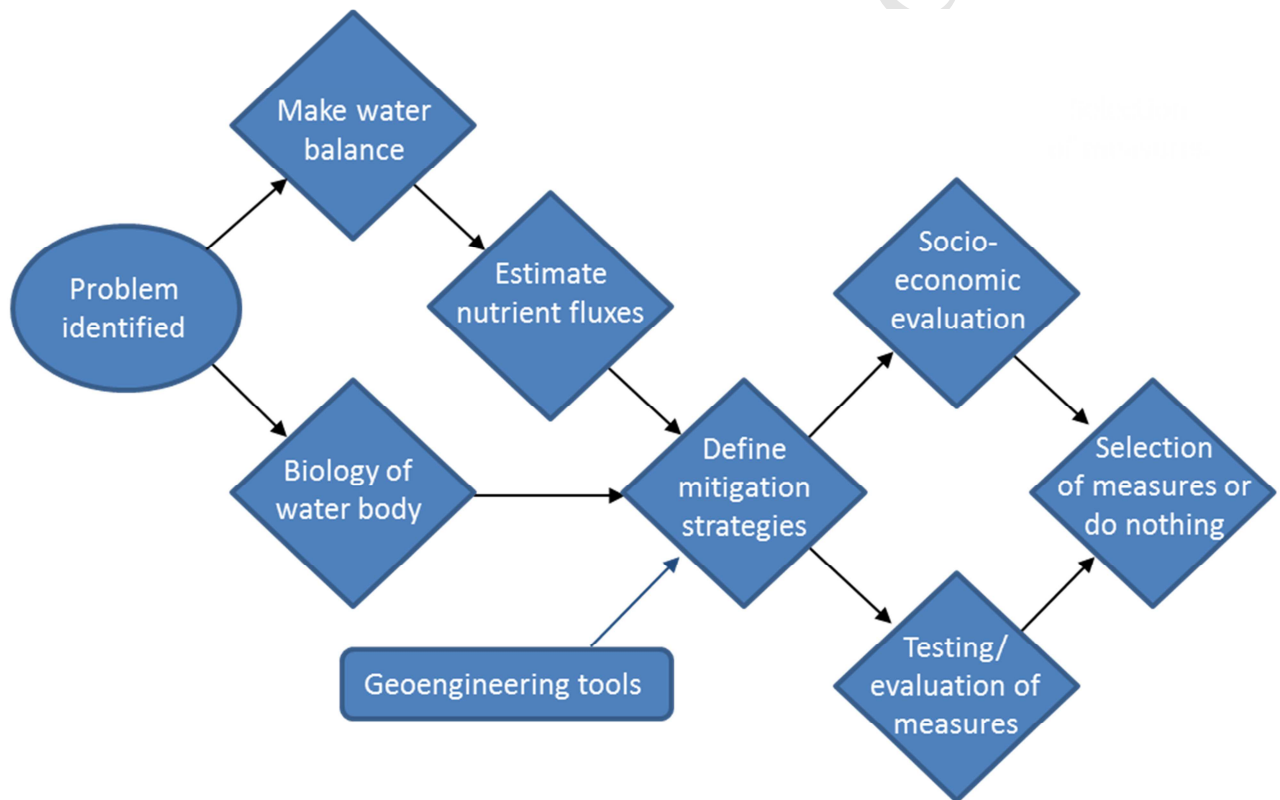
207 *Figure 3: Estimated phosphorus loadings of several sources to Pond Dongen, Pond*  
 208 *Eindhoven and Lake De Kuil, including the critical loading for the transition from a clear*  
 209 *water to a turbid water (red lines) and for the transition from a turbid water to a clear water*  
 210 *(green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

211

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

233 Lake managers, however, also need to consider other aspects such as safety and costs.  
234 The cost of maintenance management and essential effects monitoring should be assessed  
235 against the cost of doing nothing (Mackay et al., 2014). Hence, only after a SAL which  
236 preferably includes a societal cost-benefit analysis, the most promising measures can be

237 selected (Fig. 4). In this special issue, a one-box model is proposed, which is a mass balance  
 238 tool for predicting the P trend in the water under different management options that was  
 239 applied to the deep Lake Arendsee (Hupfer et al., this issue). By running different scenarios,  
 240 the authors could identify the magnitude of effects of external load reduction combined with  
 241 in-lake P inactivation as single or repeated applications (Hupfer et al., this issue). This  
 242 approach illustrates the power of a thorough SAL and an evaluation tool for testing the  
 243 expected longevity and impact of mitigation alternatives. Together with a cost-benefit  
 244 analysis the most promising set of measures can be chosen (Fig. 4).



245  
 246 *Figure 4: Once a eutrophication problem has been identified in a lake, a system analysis,*  
 247 *which includes determination of water- and nutrient balances, the biological composition of*  
 248 *the lake, socio-economic analysis on costs and benefits, and an evaluation of performance*  
 249 *and longevity of the proposed measures, will underpin the selection of measures that may*  
 250 *include geoengineering tools or leave ‘do nothing’ as an option.*

251

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

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

262

##### 263 *Aluminium*

264 Two manuscripts in this special issue focussed on Al in controlling eutrophication. The first  
265 study (Huser et al., this issue-a) described the restoration of the Minneapolis Chain of lakes in  
266 Minnesota (USA). External load reduction was inadequate to maintain good water quality in  
267 these urban lakes and in-lake alum dosing yielded variable results. Huser et al. (this issue-a)  
268 ascribed the variation in long-term effectiveness of whole-lake alum treatments to a poor  
269 understanding of the P loads to the lakes and inaccurate calculation methods for alum doses.  
270 In particular, the alum dose should be determined based on the amount of mobile P in the  
271 sediment – preferably in the upper 10 cm of the sediment (Reitzel et al., 2005; Huser et al.,  
272 this issue-b). A thorough review of 114 alum treated lakes demonstrated clearly that treatment  
273 longevity in deeper, stratified lakes was longer (mean 21 years) than in shallow, polymictic  
274 lakes (mean 5.7 years) where, for amongst other reasons, sediment disturbance by bottom  
275 feeding fishes (carp) reduced longevity of the treatment (Huser et al., this issue-b). Moderate  
276 densities of carp can increase the sediment mixed layer from 5 cm without carp to 16 cm with

277 carp and thus proliferate the amount of mobile sediment P that might be released to the water  
278 column (Huser et al., 2015). Huser et al. (this issue-b) also concluded that adequate  
279 monitoring programs are needed to yield more insight into factors affecting longevity of Al  
280 additions to lake sediments to further improve the effectiveness of future treatments.

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

284

285 *Iron*

286 Compared to Al, less field trials with Fe to inactivate P have been reported. In general, the  
287 redox sensitivity of Fe is viewed as a major drawback of using Fe in counteracting  
288 eutrophication in lakes (Cooke et al., 2005). Oxygen consumption due to bacterial breakdown  
289 of organic matter is a key process in the reduction of Fe and sulphate which may cause a  
290 strong decrease in the P-binding capacity of sediments due to the formation of  $\text{FeS}_x$  (Smolders  
291 et al., 2006). Recently however, Immers et al. (2015) reported promising results of  $\text{FeCl}_3$   
292 addition ( $33 \text{ g Fe m}^{-2}$ ) to a lake over 1.5 years, with lower P and cyanobacteria biomass, but  
293 they also indicated sulphate and DOC as confounding factors to the success of the treatment.  
294 Under aerobic conditions Fe may effectively trap P (Smolders et al., 2006). A recent study  
295 reported gradual long-term (20 years) improvements in water quality following a single bulk  
296 Fe addition, despite annual anoxic events, which diminished as a consequence of less organic  
297 matter accumulation (Kleeberg et al., 2013). Nonetheless, the slowness and dependence of  
298 such gradual organic matter decrease will not always meet the ambitions of water authorities  
299 for rapid results. Novel developments include Fe-modified clays, such as Bephos<sup>TM</sup>  
300 (Zamparas et al., 2013) and Sinobent<sup>®</sup> (Goldyn et al., 2014). The latter is an iron,  
301 magnesium, calcium and nitrate modified bentonite, which showed promising results in an

302 enclosure study (Goldyn et al., 2014). The addition of nitrate could increase the redox  
303 potential in the sediment and, thus, lower the internal loading of P from bottom sediments.

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

307

### 308 *Calcium*

309 When photosynthesis drives pH to values above pH 9.0 - 9.5 calcite will precipitate with  
310 possible co-precipitation of P (House, 1990; Danen-Louwerse et al., 1995; Cooke et al.,  
311 2005). The formed P precipitates, such as hydroxyapatite, but also calcite, have low solubility  
312 at pH higher than 9 (Cooke et al., 2005) and consequently, application of Ca to manage P is  
313 primarily suited for hard water lakes with relatively high pH, where liming could lower  
314 sediment P release substantially (Prepas et al., 2001; Zhang et al., 2001). Laboratory  
315 experiments with sediment from eutrophic German lakes showed that active calcite barriers  
316 could strongly reduce the P efflux from the sediment (Berg et al., 2004). Several calcite  
317 characteristics like grain size, specific surface and structure determine the P adsorbing  
318 capacity (Berg et al., 2004), while complexation can be hindered by organic matter and iron-  
319 ions (Dittrich et al., 2011). A combined sodium aluminate and Ca hydroxide treatment applied  
320 to the hypolimnion strongly reduced the P diffusion rates from the sediment of Tiefwareensee  
321 and caused a rapid trophic shift that lasted at least for 7 years (Wauer et al., 2009). The latter  
322 study emphasized the importance of a P balance and applied a one-box model to predict the  
323 long term outcome of the rehabilitation (Wauer et al., 2009).

324

### 325 *Lanthanum modified clay (LMB)*

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

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

346 A detailed evaluation of LMB treated lakes found reductions in surface water TP (data  
347 available from n = 15 lakes), SRP (n = 14 lakes) and chlorophyll *a* concentrations (n = 15  
348 lakes) with increased Secchi disk depth (n = 15 lakes) (Spears et al., this issue). In addition,  
349 increases in aquatic macrophyte community species numbers (average increase of 1.6 species;  
350 n = 6 lakes) and maximum colonisation depths (mean increase of 0.7 m; n = 4 lakes) were



351 reported (Spears et al., this issue). The median values of TP, SRP and chlorophyll *a*  
352 concentrations across the lakes in the 24 months following LMB application were correlated  
353 positively with pre-application DOC concentrations, suggesting DOC as a factor potentially  
354 confounding the operational performance of LMB (Spears et al., this issue). Indeed, on a  
355 short-term scale the efficacy of LMB is reduced in the presence of humic substances (Lürling  
356 et al., 2014; Dithmer et al., this issue –a). It is also likely that other oxyanions can compete  
357 with phosphate for LMB (Reitzel et al. 2013; Copetti et al., this issue). Over time the  
358 confounding effects of humic substances seem to diminish and hence LMB will slowly reach  
359 its theoretical binding capacity (Dithmer et al., this issue –a). In LMB treatments La-P mainly  
360 precipitates as rhabdophane, which was confirmed in a laboratory experiment as well as a  
361 survey of sediments from 10 LMB treated lakes in Europe (Dithmer et al., 2015; Dithmer et  
362 al., this issue –b). About 25% of the sequestered SRP was identified as surface-P adsorbed to  
363 the surface of rhabdophane, but the strength of the resultant complex remains to be  
364 determined. The sequestered P is slowly transformed from the immediately formed  
365 rhabdophane towards monazite (Dithmer et al., this issue –a). Thus, there is very strong  
366 evidence for permanent removal of P by LMB from the water and sediment P pool.

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

376

## 377 **5. Stripping cyanobacteria from the water column**

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

386

### 387 *Flocculants and ballast*

388 Flocculation and sedimentation with clay might be a cost-effective approach for  
389 controlling marine harmful algal blooms (Anderson, 1997; Sengco and Anderson, 2004).  
390 Adding a flocculent, such as polyaluminiumchloride (PAC), lowered the dose of clay needed  
391 and also improved the removal of red tide species (Sengco and Anderson, 2004; Hagström  
392 and Granéli, 2005). In fresh waters the low ionic strength of the water impairs clay  
393 flocculation of cyanobacteria (Han and Kim, 2001; Pan et al., 2006a). However, this  
394 drawback can be overcome by modifying the clay with a flocculent; addition of  $\text{Fe}^{3+}$ ,  
395 polyacrylamide or chitosan improved flocculation and removed > 90% of cyanobacteria (Pan  
396 et al., 2006b; Zou et al., 2006). Use of local sands or clays as ballast may reduce transport  
397 costs. Combined flocculent ( $10 \text{ mg L}^{-1}$  chitosan plus  $10 \text{ mg L}^{-1}$  PAC) and a local sand ( $100$   
398  $\text{mg L}^{-1}$ ) showed good removal in a laboratory experiment (Pan et al., 2011a). Likewise, Shi et  
399 al. (this issue) used cationic starch as flocculent ( $10 \text{ mg L}^{-1}$ ) that combined with a local soil  
400 ( $100 \text{ mg L}^{-1}$ ) stripped experimental jars clear of cyanobacteria, although not necessarily to

401 below safe levels for human health as indicated by the World Health Organisation (i.e. <  
402 20,000 cells ml<sup>-1</sup>). Yuan et al. (this issue) used chitosan-acidic coal fly ash leachate and coal  
403 fly ash (100 mg L<sup>-1</sup>) to flock and sink *Microcystis aeruginosa* out of the water column.  
404 Noyma et al. (this issue) showed that flocculation with either PAC or chitosan (2 mg L<sup>-1</sup>) and  
405 local red soil as ballast (160-320 mg L<sup>-1</sup>) effectively precipitated buoyant cyanobacteria  
406 harvested from a reservoir. In another laboratory experiment, Li and Pan (2015) successfully  
407 settled cyanobacteria from water using chitosan-modified local soil (2 mg L<sup>-1</sup> chitosan and  
408 100 mg L<sup>-1</sup> soil) and demonstrated reduced microcystin concentrations. Applying the  
409 flocculent-modified soil technique in the field, at 40-50 g m<sup>-2</sup> (~25-31 mg L<sup>-1</sup>), Pan et al  
410 (2011b) demonstrated the clearance of cyanobacteria from surface waters within an isolated  
411 bay (Pan et al., 2011b). The dual mechanism of surface charge and netting-bridging  
412 modification when soil or clay is modified using flocculants, yields high removal rates of  
413 cyanobacteria in both freshwater and marine environments (Li and Pan, 2013).

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

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

424

425 *Flocculants and solid-phase P fixative as ballast*

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

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

446

## 447 **6. Geo-engineering in managing eutrophication**

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

451 Waajen et al., this issue-a), there might be other reasons that warrant research on mitigating  
452 in-lake N. For instance, high inorganic N concentrations may come with toxicity issues to  
453 various aquatic organisms (Camargo et al., 2005; Camargo and Alonso, 2006), it may lead to  
454 more disease in water clearing zooplankton (Dallas and Drake, 2014) and may have negative  
455 effects on clear water stabilising macrophytes (Olsen et al., 2015). In spite of the fact that  
456 nitrate and ammonium salts are soluble and atmospheric nitrogen inputs can pose serious  
457 problems for lakes, in-lake N might be reduced partly through ammonium adsorption by  
458 zeolites (e.g., Klieve and Semmens, 1980; Wen et al., 2006). Zeolites are natural porous  
459 minerals -crystalline hydrated aluminosilicates- and strong cation absorbers (Wen et al.,  
460 2006). Zeolites can concomitantly reduce the P and ammonium efflux from sediment (Lin et  
461 al., 2011). Particularly, Al modified zeolite such as Aqual-P or Z2G1 actively remove both P  
462 and ammonium released from sediments (Gibbs et al., 2011), which makes it a very promising  
463 material for managing in-lake nutrient loads. More up-scaled research is needed as  
464 concurrently lowered in-lake N and P concentrations could also promote buffering against  
465 return to a more eutrophic state. Hence, there is a great potential for geo-engineering in  
466 controlling nuisance cyanobacteria and mitigating eutrophication.

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

476 application beyond one decade (Hupfer et al., this issue). When external P-load reductions are  
477 economically or technically difficult, curative measures should be an option.

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

493         Most engineered solid phase P-sorbents, particularly the ones addressed in this special  
494 issue, are primarily designed to target internally released phosphate from lake bed sediments.  
495 As the contributions to this special issue demonstrate, geo-engineering in lakes by use of such  
496 P-adsorptive materials or flocculants and ballast can be a powerful approach to mitigate  
497 eutrophication. Eutrophication is recognised as the most important water quality issue  
498 worldwide (Smith and Schindler, 2009; Downing, 2014), yet, eutrophication research is not  
499 listed among the top three research paradigms studied by limnology (Downing, 2014).  
500 Instead of focussing on quick fix approaches, the diversity of surface waters demand a SAL

501 guided approach to recognise the individual characteristics of each lake (Björk, 1972). Even  
 502 though the use of P-adsorptive materials is a commonly used ‘geoengineering’ approach  
 503 (Mackay et al. 2014), a multi-national collaboration and research centre to develop and test P  
 504 and/or N adsorptive materials, flocculants and ballast compounds is strongly recommended to  
 505 boost scientific insights and support the development and validation of emerging and novel  
 506 compounds, reducing time from concept to market. New geo-engineering compounds should  
 507 be effective, safe, cheap and easy to prepare and use, and an independent research and policy  
 508 body is necessary to underpin this. The first step will be demonstrating efficacy and safety  
 509 under controlled conditions (Fig. 5), moving to replicated field and ecosystem scale  
 510 experiments (Fig. 5).

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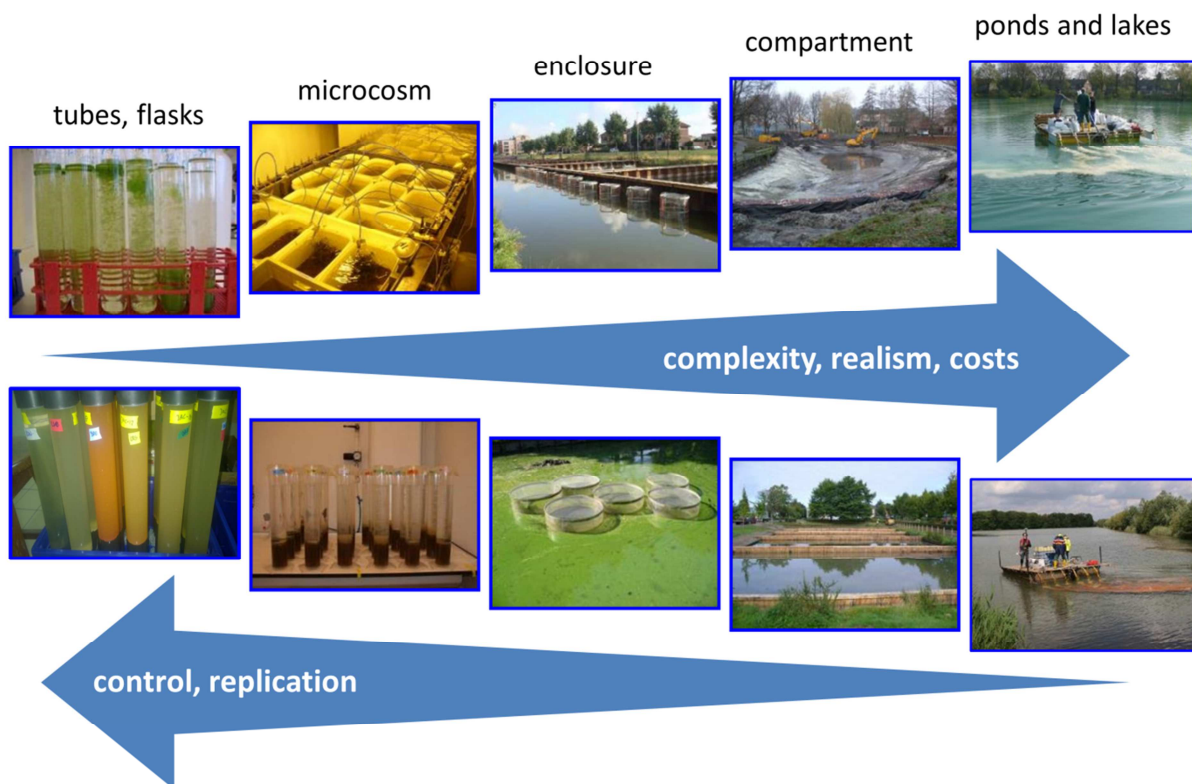
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523 *Figure 5: Research at various scales from controlled and replicated laboratorial experiments*  
 524 *to whole lake experiments yielding a powerful balance between statistical power and reality .*

525



## 526 **7. Conclusions**

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

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