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a review

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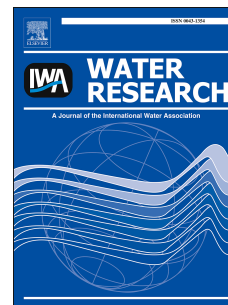
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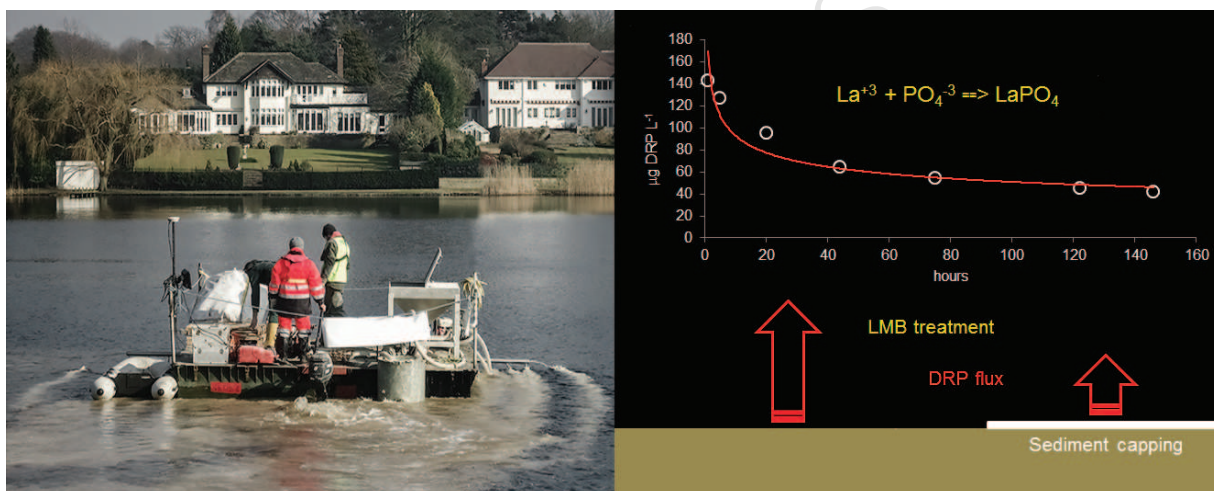
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1 **Eutrophication management in surface waters using lanthanum modified bentonite: a review**

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23

24 **Abstract**

25 This paper reviews the scientific knowledge on the use of a lanthanum modified bentonite (LMB) to
26 manage eutrophication in surface water. The LMB has been applied in around 200 environments
27 worldwide and it has undergone extensive testing at laboratory, mesocosm, and whole lake scales.
28 The available data underline a high efficiency for phosphorus binding. This efficiency can be
29 limited by the presence of humic substances and competing oxyanions. Lanthanum concentrations
30 detected during a LMB application are generally below acute toxicological threshold of different
31 organisms, except in low alkalinity waters. To date there are no indications for long-term negative
32 effects on LMB treated ecosystems, but issues related to La accumulation, increase of suspended
33 solids and drastic resources depletion still need to be explored, in particular for sediment dwelling
34 organisms. Application of LMB in saline waters need a careful risk evaluation due to potential
35 lanthanum release.

36
37 **Keywords:** lanthanum modified bentonite; toxicity; phosphorus; sediments; ecological recovery;
38 geo-engineering

39

40

41 1. Introduction

42 The control of phosphorus (P) release from bed sediments using geo-engineering materials is
43 increasing (Mackay et al., 2014). The premise is that by controlling internal P loading the
44 ecological effects of eutrophication can be rapidly reversed. A range of materials are currently
45 available for use at the field scale and an increasing number of novel materials are being proposed
46 for use (Hickey and Gibbs 2009). However, the chemical behaviour and effectiveness of these
47 materials varies and it is, therefore, important that they are comprehensively assessed using
48 laboratory and field scale trials prior to wide scale use (Hickey and Gibbs 2009; Spears et al.,
49 2013a). Since its development by the Australian CSIRO in the 1990s (Douglas et al., 1999; Douglas
50 et al., 2000), lanthanum modified bentonite (LMB), commercially known as Phoslock®, has
51 undergone extensive development and testing at laboratory, mesocosm, and whole lake scales but,
52 to date, no comprehensive review of this work has been published. This is despite the fact that LMB
53 has been applied to about 200 water bodies across a wide geographic distribution (about 50% in
54 Europe, 30% in Australia and New Zealand, 13 % in North America, 2% in Asia and 1% in Africa
55 and South America). Given the wide scale use of this material it is conspicuous that relatively few
56 reports of its efficacy appear in the peer reviewed literature (there are only 16 peer reviewed reports
57 of field scale applications of LMB), limiting the capacity of water managers to make evidence
58 based decisions on its wider application as a robust eutrophication management tool. Instead, many
59 results across a wide range of laboratory and field based trials have been documented in the ‘grey
60 literature’, these reports having been commissioned by industry and environmental regulators but
61 generally not being made more widely accessible to the scientific community.

62 To address this we draw on the experiences of a wide range of research groups who have led the
63 development and assessment of LMB for use as a eutrophication management tool to review the
64 collective evidence base. This paper addresses the following overarching questions: what was the
65 general scientific premise underpinning the development of LMB; what evidence is available at
66 laboratory, mesocosm, and field scales to support the use of LMB in lakes; and what are the

67 positive and negative environmental and human health implications of its use? We address these
68 questions by drawing on evidence from (up to March 2015) 40 peer reviewed publications and 10
69 technical reports. Three relevant papers published in this special issue were also taken into account.

70

71 **2. Early development of LMB**

72 LMB was borne from a need to develop a P (more specifically, phosphate PO_4) absorbent for
73 application to eutrophic systems that could be easily applied and was environmentally compatible in
74 terms of its physico-chemical characteristics and ecotoxicological profile. LMB was extensively
75 evaluated at laboratory, pilot and field scale prior to patenting and commercialization by CSIRO. In
76 documenting the research and development of the LMB, a range of aspects including the
77 geochemistry of lanthanides, more commonly known as the rare earth elements (REEs), their
78 commercial sources, laboratory and field trials of the LMB and patenting commercial aspects are
79 discussed below.

80

81 *2.1 Lanthanum and other rare earth elements in the biosphere*

82 Within the biosphere, few elements are known to bind strongly to PO_4 to form minerals that are
83 stable over a range of pH and redox conditions commonly encountered in natural waters. The REEs
84 form a coherent chemical series from the atomic number $Z=57$ to 71 but which also include yttrium
85 [Y] and scandium [Sc]. The majority of REEs are trivalent, however both cerium [Ce; +4, +3] and
86 europium [Eu; +2, +3] may have different redox-sensitive oxidation states. In general, the REEs
87 behave geochemically as a coherent group, however, the well-known lanthanide contraction (that
88 leads to a decline in ionic radius from 1.13 Å for La^{3+} to 1.00 Å for Lu^{3+}) confers a subtle change in
89 properties, notwithstanding the alternative Ce and Eu oxidation states. Within the group the light
90 REEs such as lanthanum [La] are by far the most abundant. By way of comparison La ($38 \mu\text{g g}^{-1}$)
91 and Ce ($80 \mu\text{g g}^{-1}$) are similar to elements such as copper [Cu; $50 \mu\text{g g}^{-1}$] and other elements like
92 cobalt [Co; $23 \mu\text{g g}^{-1}$], and lead [Pb; $20 \mu\text{g g}^{-1}$] in terms of average crustal abundance (Taylor and

93 McLennan, 1985). The light REEs also have a substantially greater natural abundance relative to
94 the heavy REEs such as ytterbium [Yb; $2.8 \mu\text{g g}^{-1}$]. Within the biosphere, the REEs may also be
95 found in a range of rocks, sediments (e.g. Moermond et al., 2001) and soils (Tyler, 2004) as well as
96 in terrestrial (Markert, 1987) and aquatic biota (Ure and Bacon, 1978; Mayfield and Fairbrother,
97 2015).

98 Sources of REEs are generally confined to two types, that of heavy mineral-enriched beach sands,
99 or primary or secondary igneous pegmatite-hosted deposits. While the environmental persistence of
100 the REE- PO_4 minerals can be considered a virtue, the often closed systems allow accumulation of
101 daughter radionuclides, often without net loss leading to a substantial activity, particularly when the
102 minerals are concentrated. In addition, separation of the radionuclides may be incomplete leading to
103 low levels of residual radioactivity associated with the REE. In the specific context of
104 environmental applications, this factor may reduce their range of practical uses. This challenge,
105 however, has largely been overcome due to the existence of the large REE deposit in Baotou,
106 located in Inner Mongolia which has been estimated to host approximately 75% of the world's
107 known REE reserves (Zhongxin et al., 1992). This deposit and the LaCl_3 produced from it is of
108 inherently low radioactivity compared to many heavy mineral-hosted REE deposits such that it is
109 often lower than that of many of the soils and bottom sediments at the sites where it is utilized.

111 2.2 *The development of lanthanum modified bentonite (LMB)*

112 There is a naturally strong affinity of La and other REEs with PO_4 . Based on its abundance and
113 single oxidation state, La, was chosen as the most prospective REE to use to explore possible
114 application in the binding of PO_4 in aquatic environments to replicate one or more of the minerals
115 commonly found in the natural environment. While a robust bond could be formed between La and
116 PO_4 , another key factor was the simple 1:1 stoichiometry without the requirement for other moieties
117 or intermediates, thus simplifying potential real world applications. Earlier research had also
118 suggested a potential for the use of La for the removal of PO_4 from wastewaters (e.g. Melnyk et al.,

119 1974). A major factor that was considered during the development of this P binding product was the
120 search for a suitable carrier-exchange system that could contain a reservoir of La available for the
121 complexation with PO_4 . This would negate the inherent toxicity associated with the dissolved
122 (“free”) La (e.g. Barry and Meehan, 2000; Oral et al., 2010) and mitigate the dilution or advection
123 in the site of application. To this end, and after considerable testing with a range of minerals, a
124 bentonite was chosen as the carrier exchange substrate (Douglas et al., 2000). Advantageously, the
125 bentonite also satisfied a number of other requirements. Being an aluminosilicate mineral, it was
126 considered compatible with application to clay-rich aquatic suspended and bottom sediments.
127 Having similar density and particles size, upon settling it could be incorporated as a seamless
128 component of the bottom sediment thus limiting physical resuspension or bioturbation.
129 Furthermore, the bentonite has an inherently low toxicity, is commercially available in large
130 quantities around the world and typically possesses a moderate to high cation exchange capacity
131 (CEC) of between 60 and 100 meq 100 g^{-1} . Correctly prepared, a typical LMB has a La
132 concentration of ca. 5% depending on the precursor bentonite CEC, a concomitant PO_4 -P-uptake
133 capacity of ca. 1%, and a low residual La concentration within the co-existing solute (Douglas et
134 al., 2000).

135

136 2.3 Preliminary laboratory and pilot-scale field trials

137 Initial laboratory trials using LMB in batch mode, aquatic sediment core incubations and within
138 small (1m diameter) and large (6m diameter) mesocosms confirmed the efficacy of the LMB as an
139 efficient PO_4 sorbent able to reduce the dissolved P load in the water column and the internal P
140 loading by reducing the sediment-derived PO_4 fluxes (Douglas et al., 1999). In particular, the
141 efficiency of the LMB in P-binding was tested on a range of sediment cores and surface waters and
142 on wastewater samples. Soluble reactive phosphorus (SRP) concentrations (initial range 120-130 μg
143 P L^{-1}) in pore water sediment cores were reduced by more than 98% in a 7 day batch-test and by 87-
144 98% in a 48 hours batch test conducted on surface water samples (initial SRP concentration range

145 20-450 $\mu\text{g P L}^{-1}$). Batch tests on wastewaters with SRP initial concentrations of 1,130 to 5,320 $\mu\text{g P}$
146 L^{-1} demonstrated removal percentages of greater than 99%.

147 In parallel with the field trials, continuing laboratory evaluation of the LMB included assessment in
148 the presence of high dissolved organic carbon (DOC) concentrations (Douglas et al., 2000). In
149 addition, extensive acute and chronic ecotoxicological testing was also undertaken using a range of
150 biota including daphnia, polychaetes and juvenile fish. All ecotoxicological testing indicated low
151 acute and chronic responses provided the LMB was correctly prepared, in particular containing low
152 concentrations of free La (Douglas et al., 2000).

153 Initial mineralogical characterization of the reaction products produced by the LMB in contact with
154 PO_4 solutions indicated the formation of rhabdophane, a hydrated mineral of the formula
155 $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ commonly found as a weathering product of REE- PO_4 minerals (e.g. Jonasson et al.,
156 1988). This confirmed the efficient 1:1 La to PO_4 binding stoichiometry and the production of a
157 mineral known to be stable across a range wide range of terrestrial and aquatic environments (e.g.
158 Nagy and Draganits, 1999).

159 Geochemical modelling undertaken using PHREEQC (Parkhurst, 2014) to assess the saturation
160 index (SI) of rhabdophane-(La) is shown in Figure 1 (Douglas et al., 2000). In freshwater and
161 seawater rhabdophane is nominally stable ($\text{SI} > 0$) between pH of ca. 5.0 and 5.5 and 9.7 and 9.3,
162 respectively. Maximum saturation is ca. 10^4 and 10^3 relative to the solution at ca pH 7.8 for
163 freshwater and seawater respectively. This modelling confirmed the wide environmental range of
164 rhabdophane formed as a result of the application of LMB to aquatic systems.

165 During laboratory-scale evaluation it was found that substantial La may be released from LMB if
166 exposed to saline environments (Douglas et al., 2000). This has two effects. In the short-term, the
167 first is to introduce a range of soluble La species into the water column with the likelihood of
168 significant ecotoxicological effects. The second medium to long-term effect, due to partial or
169 complete La loss, is to substantially reduce efficacy or render the LMB ineffective respectively as a
170 reactive layer for the absorption of labile P species at the sediment-water interface.

171 The results of this experimentation indicated that the application of the LMB in even moderately
172 saline environments of >0.5 ppt is to be avoided (Douglas personal communication).
173 A large-scale pre-commercial application of LMB was undertaken in the Canning River in
174 metropolitan Perth, Western Australia in early 2000 (Robb et al., 2003). This trial was conducted on
175 a scale commensurate with that required for the management of P in eutrophic aquatic systems and
176 demonstrated the efficacy of the LMB in reducing both initial water column SRP concentrations
177 and internal sediment-derived loading. The Australian and international patents were lodged and a
178 commercial partner to exploit the intellectual property developed by CSIRO, was identified and
179 engaged.

180

181

182 Figure 1. Modelled Saturation Index (SI) for the formation of rhabdophane ($\text{LaPO}_4 \cdot n\text{H}_2\text{O}$) in
183 freshwater and seawater between pH 4 and 10.

184

185 3. Evidence of LMB use for the control of P in lakes leading to ecological recovery

186

187 3.1 LMB laboratory studies - P binding efficiency and confounding factors

188 Solid state ^{31}P NMR studies of the binding between phosphate and La, have shown that
189 rhabdophane ($\text{LaPO}_4 \cdot \text{H}_2\text{O}$) is formed initially after adding the LMB to the water. In addition to that
190 directly bound within the rhabdophane-(La), around 20% of the SRP bound by the LMB can be
191 found as adsorbed onto the rhabdophane surface (Dithmer et al. 2015). However, aging of the
192 rhabdophane may lead to the formation of monazite (LaPO_4) which has an even lower solubility
193 than rhabdophane (Cetiner et al., 2005; Dithmer et al., 2015). The behaviour of the lanthanum
194 phosphate minerals is thus markedly different from that of aluminium hydroxides, which may lose
195 more than 50% of their initial P binding capacity upon aging (e.g. Berkowitz et al., 2006).
196 Several studies have indicated La:SRP binding ratios above the expected stoichiometric ratio of 1:1,
197 suggesting interference in the rhabdophane formation. Using waters from Danish lakes Reitzel et al.
198 (2013a) found that the LMB performed better in soft waters compared to hard waters and concluded
199 that carbonate was probably competing with phosphate for binding onto La (Johannesson et al.,
200 1995). However, a recent study performed in lake and pore water from 16 Danish lakes with
201 varying alkalinities, did not show any correlation between alkalinity and P binding capacity of the
202 LMB (Dithmer et al., this Issue). Instead, a significant negative correlation was found between lake
203 water DOC concentrations and SRP binding capacity of the LMB, demonstrating that DOC
204 interferes with the rhabdophane formation. This result supports the findings by different authors
205 (e.g. Douglas, 2000 and Lürding et al., 2014) who observed constrained P removal by LMB in soils
206 and waters rich in DOC. In particular, Lürding et al., 2014 conducted laboratory controlled
207 experiments where the efficiency of the LMB was verified in the presence and in the absence of
208 humic substances. The authors found that in both short (1 day) and long term (42 day) experiments
209 the efficiency of LMB was reduced in the presence of humic substances. In the presence of 10 mg

210 L⁻¹ DOC the authors also found a strong increase of filterable La that in a week reached values
211 higher than 270 µg La L⁻¹. However, recent findings have demonstrated that given enough time
212 SRP will eventually be bound to the La, thereby overcoming the interference by DOC (Dithmer et
213 al., this issue).

214 Ross et al. (2008) reported a reduction of the adsorption capacity in algae-containing lake water
215 compared to water solutions prepared using reverse osmosis to remove algae. Ross et al. (2008)
216 reported that LMB did not release P under anoxic conditions. In relation to oxygen dynamics at the
217 sediment-water interface, Vopel et al. (2008) found that the LMB created a barrier between the
218 sediment and the water, promoting anoxic conditions below the LMB layer. However, it has to be
219 underlined that these results were obtained in the laboratory while in the field the mixing of the
220 surface sediment should prevent the formation of this anoxic layer (Dithmer et al. this issue).

221 Laboratory investigations on the effect of pH on the binding of PO₄ by LMB indicated maximum
222 efficiency in a pH range of 5-7 with absorption capacity decreasing at pH higher than 9 (Figure 1
223 and Ross et al., 2008; Haghseresht et al. 2009). The greatest affinity was found for the H₂PO₄¹⁻
224 monovalent phosphate ion. Similar results were found by Zamparas et al. (2012) who compared the
225 P-binding efficiency of the LMB with that of an unmodified bentonite (Zenith-N) and iron modified
226 bentonite (Zenith-Fe). The authors indicated maximum P-binding efficiency in a 6-7 pH range.
227 Both modified bentonites showed less pH-dependence than the natural bentonite. Reitzel et al.
228 (2013a), showed that increasing the pH to 9 reduced the formation of rhabdophane, compared to an
229 experiment conducted at pH 7 because of increased hydroxylation of the La at pH 9 (Haghseresht et
230 al., 2009). However, exposing P-saturated LMB to pH 9 did not lead to a significant release of P,
231 confirming rhabdophane stability. This has important implications for the use of the LMB since it
232 will be possible to dose the LMB to high pH (>9) waters, as long as the sediment pH is around
233 neutral.

234 In relation to the P binding efficiency of LMB in bed sediments, Reitzel et al. (2013b) performed a
235 35 day incubation experiment using sediment cores from a Danish eutrophic lake. A sequential

236 extraction of P and La conducted after the incubation period underlined a reduction of the iron-
237 bound P concentrations and an increase in the HCl-exchangeable P concentrations in the sediments
238 treated with the LMB. Most of the La was found in the HCl extract or the residual extract indicating
239 that P remained strongly bounded to La in the LMB matrix. In laboratory experiments Gibbs et al.
240 (2011) found a small increase of filterable aluminum (Al) associated with the use of four different
241 capping agents. The authors interpret that these variable Al concentrations may have been generated
242 by ebullition through the capping layer within the incubation chambers. Further, an enhancement of
243 ammonium release under aerobic conditions in the LMB treated incubation chambers was
244 measured. Gibbs et al. (2011) attribute this to an effect on the nitrification process, but, as ebullition
245 probably occurred, the higher ammonium concentrations could also partly derived from entrainment
246 of pore water by ebullition.

247

248 3.2 LMB mesocosm trials - evidence of P control

249 Results from mesocosm trials have been published in four studies including a reservoir in Mexico
250 (Valle de Bravo reservoir; Márquez-Pacheco et al., 2013), lakes/ponds in Italy (Lago di Varese;
251 Crosa et al., 2013), the Netherlands (De Ploeg; Lürling and Faasen, 2012) and Australia (Lake
252 Monger; Douglas et al., 1999). All studies assessed the uptake of SRP by LMB in the water column
253 and additional information regarding the effects of the treatment on other water quality parameters
254 and on toxic cyanobacteria (Douglas et al., 1999; Lürling and Faasen, 2012, Márquez-Pacheco et
255 al., 2013) as well as on the potential ecotoxicological effects of LMB (Crosa et al., 2013) were
256 provided.

257 In Lake Varese (Crosa et al., 2013) monthly sampling documented a substantial reduction the P
258 concentration in the water column after the LMB application. Mean annual concentrations of total
259 phosphorus (TP) and soluble reactive phosphorus (SRP) in the bottom water of the treated
260 mesocosm dropped down from 0.11 mg P L^{-1} to 0.04 mg P L^{-1} and from 0.09 mg P L^{-1} to 0.02 mg
261 P L^{-1} , respectively. Moreover, at the end of the 11 months monitoring period TP and SRP

262 concentrations in the bottom water of the treated mesocosm were significantly lower compared to
263 the untreated site, showing a reduction of more than 80% of the TP and SRP concentrations in the
264 water column after the LMB application. The La^{3+} concentrations were below $5 \mu\text{g L}^{-1}$ one month
265 after the application. Similar results were obtained by Márquez-Pacheco et al. (2013) who observed
266 a 75 % reduction of SRP concentrations in the water column applying a dose of LMB/TP of 40:1
267 within 18 days after the application. A 100:1 dose rate was sufficient to control SRP release from
268 the sediment during the whole monitoring period of 42 days, whereas a dose of 15:1 was sufficient
269 to reduce SRP concentrations by 25-50% for up to 15 days. In line with these results, Douglas et al.
270 (1999) observed a rapid reduction of water column SRP concentrations, reaching $5 \mu\text{g P L}^{-1}$ within
271 the first 24 hours after the application of the LMB. In the treated mesocosm the reduction of the
272 SRP concentration was sustained for up to 73 days, whereas SRP concentrations in the control
273 mesocosm exceeded 3.5 mg P L^{-1} by day 73. The reduction of SRP and TP during the monitoring
274 period reached 94-100% and 83-96%, respectively. Different results are presented by Lüring and
275 Faasen (2012) for a trial in a small urban pond. Over the whole monitoring period of 58 days,
276 median TP and SRP concentrations in the LMB treated mesocosms were 0.58 mg P L^{-1} and 0.095
277 mg P L^{-1} , respectively and did not differ substantially from the control sites (median TP 0.69 mg P
278 L^{-1} and P $0.09 \text{ mg SRP L}^{-1}$). It was surmised that the P absorption capacity of LMB in this study
279 could have been impaired by environmental factors such as pH and interference of humic acids.

280

281 3.3 LMB field trials

282 3.3.1 LMB field trials – evidence of P control in the water column

283 The first full scale application was conducted by Robb et al. (2003) in two impounded river sections
284 in Western Australia (Canning and Vasse Rivers). The authors found a marked reduction of SRP
285 concentrations in the treated areas compared to untreated areas, in both systems. For the Canning
286 River the mean summer TP concentrations dropped by 45% with the LMB treatment. A higher
287 reduction (59%) was observed in the Vasse River by the summer application.

288 Similar results were recorded during a restoration project in Lake Rauwbraken, The Netherlands,
289 using a combination of LMB and a low dose flocculent (Van Oosterhout and Lürling, 2011). The
290 treatment reduced the TP concentrations in the water column more than 90% for up to 5 years
291 (Lürling and van Oosterhout, 2013a).

292 The LMB treatment of the Dutch lake Het Groene Eiland, which was created in winter 2008 after
293 construction of three dykes which isolated this swimming area from the surrounding water body,
294 had no or only a marginal effect on TP and SRP concentrations (Lürling and van Oosterhout,
295 2013b). The mean TP and SRP concentrations in the treated and the surrounding lake were similar.
296 Confounding factors proposed were: interference with other oxyanions and humic substances,
297 uneven distribution over the sediment and continuous P input from groundwater and overwintering
298 waterfowls. This case underpins that a thorough system analysis aimed at finding the cause(s) of the
299 problem should always precede interventions, as knowledge of the causes will significantly increase
300 the chances for adequate problem solving. This implies a full investigation of the water and nutrient
301 flows –both water related and unrelated-, the biological make-up of the system and the societal
302 environment related to the functions of the specific water.

303 Very high removal efficiency (80-95%) of TP and SRP within 2 weeks after LMB treatment were
304 reported by Bishop et al. (2014) for the Laguna Niguel Lake, California, USA.

305 Haghseresht et al. (2009) reported a TP and SRP reduction ranging from 85 to 99% in a Nursery
306 Dam (Australia). Liu et al. (2009) in Lake Dianchi (China) reported a rapid decline in TP and SRP
307 concentrations falling below the detection limit. Finally, in a pilot treatment of the LMB conducted
308 in the artificial river ALA (China) Liu et al. (2012) reported a removal rate of the SRP about 97%.

309 A decrease in annual mean TP concentrations (about 50%) was also shown for lowland, high
310 alkalinity and eutrophic Loch Flemington, Scotland, (Gunn et al., 2014) by the application of LMB.

311 Spears et al. (this issue) assessed the responses in TP and SRP across multiple treated lakes (15 for
312 TP and 14 for SRP) in the 24 months following LMB applications. TP concentrations across the
313 lakes decreased markedly from a median of 0.08 mg P L^{-1} in the 24 months pre-application to 0.03

314 mg P L⁻¹ in the 24 months after the post-application. TP concentration reduction was most evident
315 in autumn (from 0.08 mg P L⁻¹ to 0.03 mg P L⁻¹) and winter (from 0.08 mg P L⁻¹ to 0.02 mg P L⁻¹).
316 Decreases in SRP concentrations from 0.019 mg P L⁻¹ to 0.005 mg P L⁻¹ were reported at an annual
317 frequency with the strong responses being reported in summer (0.018 mg P L⁻¹ to 0.004 mg P L⁻¹),
318 autumn (0.019 mg P L⁻¹ to 0.005 mg P L⁻¹) and winter (0.033 mg P L⁻¹ to 0.005 mg P L⁻¹).
319

320 Table 1. Summary of data reported for the aquatic systems cited in the review. SA=surface area, MD=max. depth,
 321 AD=average depth, WV=water volume, LMB=lanthanum modified bentonite, PAC= polyaluminium chloride

Name	Country	Waterbody	Morphometry	Year of application	LMB (t)	LMB (kg m ⁻²)	Reference
Laguna Niguel Lake	USA	Reservoir	SA=0.124 km ² ; MD=9.5 m AD=3.7 m	2013	51.34	0.414	Bishop et al., 2014
Cane Parkway	Canada	Stormwater pond	SA= 0.0043 km ² AD=2 m	2008	-	-	Moos et al., 2014
Scanlon Creek Reservoir	Canada	Reservoir	SA=0.034 km ² ; AD=7 m	2008/2009	18	0.53	Moos et al. 2014
Lake Dianchi	China	Trial pond	SA=0.002 km ² ; MD=11 m AD=5 m	2006	10	5	Liu et al. 2009,
ALA River	China	Artificial river section	S =0.008 km ² ; AD=2.5 m	2010	4	0.5	Liu et al., 2012
Canning River	Australia	Impoundet river section	MD<3 m	2001/2002	45	-	Robb et al., 2003; Novak and Chambers, 2014
Vasse River	Australia	Impoundet river section	MD<3 m	2001/2002	40	-	Robb et al. 2003; Novak and Chambers, 2014
Nursery Dam	Australia	Dam	WV=10,000 m ³	NA	4	-	Haghseresht et al., 2009
Uki	Australia	Waste water treatment pond	SA=0.0014 km ² ; AD=1 m	2008	-	-	Moos et al. 2014
Cable Ski Logan	Australia	Constructed pond	SA= 0.04 km ² AD=2 m	2008	20	0.5	Moos et al. 2014
Lake Rauwbraken	Netherlands	Sand excavation lake	SA=0.04 km ² ; MD=15 m	2008	18 t LMB 2 t PAC	0.45 LMB 0.05 PAC	Lürling and van Oosterhout, 2013a
Het Groene Eiland Loch	Netherlands	Sand excavation lake	SA=0.05 km ² MD=4.5 m AD=2.5 m	2008/2009	14.1	0.282	Lürling and van Oosterhout, 2013b
Flemmington	UK	Natural lake	SA=0.15 km ² ; MD=2.9; AD = 0.75 m	2010	25	0.159	Meis et al., 2013; Gunn et al., 2014
Clatto Reservoir	UK	Reservoir	SA=0.09 km ² ; AD=2.8 m	2009	24	0.267	Meis et al. 2012

322
 323 *3.3.2 LMB field trials – impacts on sediment P properties*

324

325 The efficiency of the LMB in P binding in sediments has been evaluated in a number of studies. In
 326 laboratory and field experiments Liu et al., 2012 investigated the different P forms present in
 327 sediments and analysed their contributions to the P loadings of the artificial river ALA (China). A
 328 pilot project was pursued with the dose rate of LMB at 0.5 kg m⁻², in a section of the artificial river,
 329 with successive applications every three months, with a P-inactivation rate of the bed sediments
 330 reaching 31% after 1 year. Similar results were reported by Meis et al. (2012) in Clatto Reservoir,
 331 Scotland. 28 days following an application of LMB a significant increase of sediment La
 332 concentration in the upper 8 cm was found, indicating that LMB was transported deeper in the

333 sediment and a significant increase in the 'residual P' fraction in the top 2 cm of sediment was
334 reported. Other sediment P-fractions, including P_{mobile} , did not differ significantly. Sequential
335 extraction of P from saturated sediments by LMB under laboratory conditions indicated that around
336 21% of P bound by LMB was release-sensitive, while the remaining 79% was unlikely to be
337 released even under reducing conditions in shallow lakes.

338 In a long term study with sediment cores collected before and after LMB application in the Scottish
339 lake, Loch Flemington, Meis et al., 2013 quantified the effects on elemental composition and P-
340 binding properties estimating that the applied mass of La would be sufficient to bind approximately
341 25% of P_{mobile} in the top 4 cm. The mass of P present in the 'apatite bound P' fraction increased
342 over time during the post-application period and was significantly higher after 12 months,
343 indicating that LMB influences sediment P release by increasing the mass of P permanently bound
344 in the sediment. Likewise in the Dutch Lake Het Groene Eiland, Lüring and van Oosterhout,
345 (2013b) reported a reduction of about 50% of 'labile' P-pool, with a reduction of about 25% one
346 month after application. Also in the sediment of Laguna Niguel Lake, California (Bishop et al.,
347 2014) the sediment P fractions were significantly different between pre-treatment and after 3-month
348 post-treatment, with reductions of the labile, reducible-soluble, and organic P fractions and
349 significant increase of the metal-oxide, the apatite and the residual fractions, with an evident shift of
350 phosphorus fractions to less bioavailable forms.

351 352 3.3.3 LMB field trials – evidence of wider ecological responses

353 There are few analyses of the recovery trajectories of ecological communities in LMB-treated lakes,
354 so that a general review of evidence of ecological responses at different levels can be done only
355 partially.

356 In Loch Flemington, monthly monitoring of the phytoplankton community was conducted 10
357 months before and 20 months after a 170 g m^{-2} LMB application (Meis, 2012). Phytoplankton
358 biomass decreased significantly the first season after the treatment, in correlation with P

359 concentration. On the contrary, changes in relative class abundances were found from the second
360 season, and indicated a decrease of Cyanophyceae and an increase of Dinophyceae and
361 Chlorophyceae.

362 Similarly, Bishop et al. (2014) reported a strong reduction of Cyanophyceae and an increase of
363 Bacillariophyceae and Chlorophyceae in the 6 months following a 112 mg L⁻¹ LMB treatment in
364 Laguna Niguel lake, California. The pre-treatment algae assemblage was dominated by
365 Cyanophyceae (primarily *Aphanizomenon flos-aquae*) with an average density of 33,300 cells mL⁻¹.
366 After the treatment the Cyanophyceae showed a very low density (average of 1,200 cells mL⁻¹) and
367 the algae populations were dominated by Chlorophyceae and Bacillariophyceae (average 6,000
368 cells mL⁻¹). Scum formation was not observed and no algaecide applications were required for
369 cyanobacteria control in 2013.

370 A marked decrease in the Chl-a concentrations was detected in the Vasse River. Chl-a
371 concentrations remained similar in both sites of the Canning River characterized by alternating
372 dominance in phytoplankton-macrophyte and where surface nutrient inputs were more pronounced
373 (Robb et al., 2003). To explain this contradiction Novak and Chambers (2014) studied the
374 hysteresis between macrophytes and algae in both Canning and Vasse rivers using long term data.
375 For the Canning River it was apparent that the treatment had a significant effect on reducing the
376 Chl-a concentrations with rare events of algal blooms since 2005. In the Vasse River the recorded
377 summer Chl-a values were higher than Canning, both in the control and treatment site (about 40 µg
378 L⁻¹), but on the long term (1996-2007) the river was dominated by phytoplankton blooms,
379 confirming the different response of the two systems as underlined by Robb et al., 2003.

380 In Lake Rauwbraken a marked reduction (5 times) of the Chl-a concentrations was detected and the
381 lake shifted from an eutrophic-hypertrophic to an oligo-mesotrophic condition. A surface scum of
382 *Aphanizomenon flos-aquae* present in the south-western part of the lake was successfully
383 precipitated and a deep water abundant *Planktothrix rubescens* assemblage was removed. The study
384 also evaluated the effect of the treatment on *Daphnia galeata*. In this lake a long term post-

385 treatment monitoring has been conducted between 2008 and 2014 and allowed to verify the stability
386 of the achieved oligo-mesotrophic condition (Lürding unpublished data).

387 These patterns were congruent with a relevant number of shallow lake restoration studies (Jeppesen
388 et al., 2005). A different approach, based on a paleolimnology, was used to evaluate the evolution
389 of four small waterbodies after a LMB treatment, in comparison to the pristine diatom communities
390 (Moos et al., 2014). In lakes with low water residence times and continued P load from external
391 sources, the effect of LMB tends to rapidly decline, and the need for repeat applications within a
392 short period is required. On the other hand, in more stable systems diatom communities responded
393 mostly to drivers other than P reduction, such as climatic variations.

394 One of the most evident and rapid improvements following phytoplankton biomass reduction is an
395 increase in water clarity, which determines the response of aquatic macrophytes. Gunn et al. (2014)
396 reported an increase in water clarity during summer (increase in Secchi disk depth from < 0.5 m to
397 1.4 m following application) two years after LMB treatment accompanied by a reduction of Chl-a
398 concentrations from an annual mean of $51 \mu\text{g L}^{-1}$ to $12 \mu\text{g L}^{-1}$, respectively, in the two years
399 following the application. Gunn et al. (2014) also reported a marginal increase in the number of
400 species and colonisation depth of aquatic macrophytes. Gunn et al. (2014) concluded that the lack
401 of response in macrophyte community structure may have been confounded by either the presence
402 of two exotic species (*Elodea canadensis* in particular) or as a result of a lag time (i.e. greater than 2
403 years) between improvements in water quality and the occurrence of macrophyte responses.

404 Novak and Chambers (2014) investigated the responses of macrophyte communities in two south-
405 western Australian impounded rivers. In the Canning River ($50 \mu\text{g TP L}^{-1}$) since 2005 a near
406 permanent switch to macrophyte dominance occurred, but a long recovery trajectory (about six
407 years) and a significant external intervention, namely water level manipulation, were required to
408 favour the onset of a stable macrophyte coverage. In the Vasse River no submerged macrophytes
409 were observed in the years between 1996-2007, due to the persistence of a high trophic condition
410 ($150 \mu\text{g TP L}^{-1}$) and to the pre-treatment absence of potential macrophyte colonizers. This study

411 supported thresholds of $150 \mu\text{g TP L}^{-1}$ indicating a high risk of macrophyte loss, $100 \mu\text{g TP L}^{-1}$ for
412 maintenance of existing macrophyte beds, and lower than $100 \mu\text{g TP L}^{-1}$ for restoration of a diverse
413 macrophyte community via transplantation for shallow, still waters. Novak and Chambers (2014)
414 deduced that the efficacy of these thresholds is dependent on phosphorus limitation. Moreover, they
415 suggested that multiple interventions, together with LMB treatment might be required to achieve
416 the restoration goals.

417 The 'Flock & Lock' treatment of iron(III)chloride and LMB in Lake De Kuil (The Netherlands)
418 caused a noticeable increase in macrophyte coverage from virtually no macrophytes to almost 12%
419 area coverage two years after the treatment (Waajen et al., this issue). *Elodea nuttallii* and *Chara*
420 *vulgaris* became dominant over time and also filamentous macro-algae made up a substantial part
421 of the aquatic vegetation of Lake De Kuil (Waajen et al., this issue).

422 Considering consumer community trends, any significant change either in structure, or in biomass,
423 in fish or zooplankton communities was not detected in the above cited case of Loch Flemington
424 (Meis, 2012), but the high uncertainty associated with monitoring fish makes detection of field
425 scale responses difficult, especially over relatively short time scales. In Lake Rauwbraken
426 (Netherlands), after a 'Flock and Lock' treatment using a combination of PAC and LMB the
427 zooplankton *Daphnia galeata* temporarily disappeared from the water column one week after the
428 application, and reappeared after three months (Van Oosterhout and Lurling, 2011). Moreover, the
429 loss of one generation of perch (*Perca fluviatilis*) was demonstrated. Nonetheless these effects were
430 temporary. In this case, the disappearance of the cladoceran *Daphnia galeata* was related to a
431 combination of physical effects of flocks, grazing inhibition of flocks and clay, abatement of food
432 resources and absence of refuge from predation. An acute toxicity of LMB components or
433 aluminum, used together with LMB under the "Flock and Lock" technique was excluded.

434 A single study (Bishop et al., 2014) investigated the resident benthic community variation in terms
435 of taxa richness, diversity, tolerance and functional feeding group composition upstream, in the
436 inflow, and downstream, in the outflow, of Laguna Niguel lake, California. No substantial

437 variations were found before and for four days after the LMB application (approximately 112 mg
438 LMB L⁻¹).

439 440 **4. Implications of LMB use for environmental and human health**

441 442 *4.1 Evidence from ecotoxicological studies*

443 The toxicity of LMB has been investigated for a range of aquatic organisms (Table 2). In particular,
444 toxicity has been estimated by exposing organisms directly to LMB (Lürling and Tolman, 2010;
445 Van Oosterhout and Lürling, 2011; Van Oosterhout and Lürling, 2013), to LMB leachates (Van
446 Oosterhout and Lürling, 2013) or to its active component lanthanum using lanthanum salt solutions
447 (Barry and Meehan, 2000; Borgmann et al., 2005; Lürling and Tolman, 2010; Xu et al., 2012; Van
448 Oosterhout and Lürling, 2013).

449 A few experiments have assessed the direct toxicological effects of LMB on aquatic organisms,
450 such as *Ceriodaphnia dubia*, the fish *Melanotaenia dubolayi* and *Oncorhynchus mykiss*, and the
451 benthic invertebrates *Macrobrachionum* sp. (Crustacea), *Hexagenia* sp. (Ephemeroptera) and
452 *Chironomus zealandicus* and *Chironomus dilutus* (Diptera) (Stauber 2000; Stauber and Binet 2000;
453 Ecotox 2006a; 2006b; 2008; Watson-Leung 2009). Most trials are acute tests and results are
454 published only in reports, a number of which were already summarized by Groves (2010) and
455 Spears et al. (2013b). In particular, little information is present in peer-reviewed literature on the
456 potential effects of LMB applications on benthic invertebrates, i.e. sediment-dwelling organisms
457 which may experience the highest turbidity and La concentrations and may be directly exposed to
458 the lanthanum modified clay through ingestion and bioturbation (Lürling and Tolman 2010; Reitzel
459 et al., 2013b; Spears et al., 2013b).

460 Remarkably few studies have assessed the ecotoxicological effects of LMB on primary producers in
461 the form of macrophytes or algae. At doses above 0.5 g L⁻¹ LMB growth rates of both the green
462 alga *Scenedesmus obliquus* and the cyanobacterium *Microcystis aeruginosa* were strongly

463 hampered (Van Oosterhout and Lürling, 2013). LMB leachates had little effect on growth of these
464 organisms and also the effect of La concentrations comparable to La in the LMB doses had much
465 less effect on phytoplankton growth. The authors ascribed the larger effect of LMB to the presence
466 of the bentonite particles (Van Oosterhout and Lürling, 2013).

467 When assessing the toxicity of LMB, it has to be considered that the effect may be related not only
468 to the potential release of La³⁺ ions, but also to a physical effect of clay on the organisms living
469 within the receiving waters. At the field scale, one target effect is the reduction of phytoplankton
470 biomass as a result of flocculation, precipitation and P reduction (Lürling and Tolman, 2010; Van
471 Oosterhout and Lürling, 2013). However, other non-target effects have been reported. Laboratory
472 experiments have demonstrated a reduced grazing activity of *Daphnia galeata* (Van Oosterhout and
473 Lürling, 2011); this may be caused by the initial high turbidity, which is known to reduce feeding
474 rates in *Daphnia* (e.g. Kirk, 1991); or it could be associated with the reduced Chl-a values, i.e.
475 lower food availability. The latter explanation is supported by the experiments by Lürling and
476 Tolman (2010), who found that in the presence of phosphorous the formation of rhabdophane in a
477 test solution of lanthanum nitrate caused a precipitation of algae (added as food), with a consequent
478 reduction in *D. magna* growth. Population growth rate for the planktonic rotifer *Brachionus*
479 *calyciflorus* was reduced at LMB concentrations of 200 mg L⁻¹ or higher (Van Oosterhout and
480 Lürling, 2013). As LMB concentrations during and shortly after the surface addition from a barge
481 will be much higher than the estimated EC₅₀ (half maximal effective concentration) for growth
482 inhibition (154 mg L⁻¹), a field application of LMB may have a negative effect on rotifers. In
483 general terms, Spears et al. (2013b) defined on the basis of the cited 16 case studies the range of
484 observed values of suspended solids (0.62-46.0 mg L⁻¹) estimated during an LMB application,
485 which overlaps the concentrations found to cause significant effects on a wide range of organisms
486 (Bilotta and Brazier, 2008). These values, although temporary, may be not compatible with the
487 water quality standards for short term exposure (24 h) defined by Canadian, EU or USA
488 regulations, expressed as increased concentrations relative to background levels and ranging from 2

489 to 25 mg L⁻¹. There is a need, therefore, for further assessment of the physical effects of LMB on
490 aquatic organisms, considering also exposure duration and frequency, which strongly determine the
491 overall effect of suspended solids. Even though suspended solid concentrations can reach pre—
492 application conditions rapidly after an application; short-term durations of elevated concentrations
493 following an application are theoretically sufficient to impair productivity in macrophytes and
494 algae, or to cause mortality of young fish (Bilotta and Brazier, 2008). In general, major effects may
495 be hypothesized for lithophilic fish species, especially if suspended solid deposition occurs during
496 the reproductive phase, egg development or fry growth (November-January for salmonids, but also
497 spring for lithophilic cyprinids). On the contrary, effects on cladoceran or copepod species were
498 demonstrated for concentrations one order of magnitude higher than those usually occurring during
499 LMB applications (Bilotta and Brazier, 2008). Concerning the effects of turbidity on benthic
500 organisms, available information is usually biased towards lotic ecosystems, and the little
501 information available for lakes is not sufficient to draw any conclusion. In Loch Flemington, a
502 reduction of abundance of Chironomidae, Oligochaeta and Sphaeriidae, together with an increase of
503 Trichoptera (Meis, 2012), were observed in the first year after LMB application. Nevertheless, the
504 role of fine inorganic sediment deposition could not be disentangled from other possible effects,
505 such as the reduction of trophic status, or direct La toxicity in this field study.

506 Toxicity has been evaluated also in terms of responses to leachate La, after a LMB treatment.
507 Concentrations of filterable La during and shortly after application may be much higher than the
508 estimated thresholds (Van Oosterhout and Lürling, 2013). For example, according to Van
509 Oosterhout and Lürling (2011), the maximum Filterable La (FLa) concentration measured in Lake
510 Rauwbraken was 90.8 µg FLa L⁻¹, which is close to the estimated chronic NOEC (No observed
511 effect level) on reproduction for *Daphnia magna*, with potential effects on reproduction. As well,
512 the average concentration of LMB in the lake was 67 mg L⁻¹ during application, a value close to the
513 concentrations affecting growth in juvenile *Daphnia* after 5 days exposure (> 100 mg L⁻¹ according
514 to Lürling and Tolman, 2010). Spears et al. (2013b) reviewed La concentrations during and after

515 LMB applications in 16 lakes. FLa values in surface water reached peaks up to 0.414 mg La L⁻¹,
516 exceeding for example the 48 h-EC₅₀ for *Ceriodaphnia dubia* of 0.08 mg La L⁻¹ but not the 48 h-
517 EC₅₀ of 5.00 mg La L⁻¹ found by Stauber (2000) and Stauber and Binet (2000). FLa values were
518 higher in surface waters than in bottom waters (peaks up to 0.100 mg La L⁻¹), but at present
519 information on toxicity of La for benthic organisms is scarce. Spears et al. (2013b) reported on the
520 LMB, Total La (TLa) and FLa concentrations occurring in the surface and bottom waters of 16
521 treated lakes. Maximum surface water of TLa and FLa concentrations ranged between 0.026 mg L⁻¹
522 and 2.30 mg L⁻¹ and 0.002 mg L⁻¹ to 0.14 mg L⁻¹, respectively. Chemical equilibrium modelling
523 indicated that the concentrations of La³⁺ ions never exceeded 0.0004 mg L⁻¹ in lakes of moderately
524 low to high alkalinity (>0.8 mEq L⁻¹), but that La³⁺ concentrations had the potential to reach 0.12
525 mg L⁻¹ in lakes characterised by very low alkalinity.

526 Taken together, the above studies show that a huge range of ecotoxicological responses across a
527 wide range of taxa has been reported for both La and LMB (Table 2). This variability could be
528 related, for example, to different media and experimental settings, to filtration protocols, and to the
529 presence of oxyanions or humic substances which may lower the bioavailability of La (Lürling and
530 Tolman, 2010; Spears et al., 2013b). Therefore, when considering the potential application of LMB
531 to a lake, preliminary trials using water collected from the target water body are recommended, in
532 particular for soft-waters.

533 Another concern is the potential release of other toxic substances from the LMB. For example,
534 some authors found the release of trace metals (Lürling and Tolman, 2010) and NH₄⁺ (Reitzel et al.
535 2013b, Van Oosterhout and Lürling, 2013) in the LMB leachate, therefore, further investigation is
536 needed in order to assess the release of impurities in natural waters. Nonetheless, according to the
537 present knowledge, post application adverse effects caused by eventual impurities have not been
538 reported.

539 Some experiments have focused on the potential bioaccumulation of La in aquatic organisms. Van
540 Oosterhout et al. (2014) treated *Procambarus fallax f. virginialis* with an application of 1 g LMB L⁻¹

541 and measured the bioaccumulation of La in the crayfish after 14 and 28 days. They found a strong
542 increase in concentrations in the ovaries, hepatopancreas and abdominal muscle, showing that La
543 released from LMB is bioavailable for crustaceans. The uptake may occur through permeable body
544 surface, gills and/or contaminated food. La bioavailability was found for the duckweed *Sperolletta*
545 *polyrrhiza*, the frogbit *Hydrocharis dubia*, *D. magna*, the shellfish *Bellamya aeruginosa* and
546 goldfish exposed to lanthanum nitrate, with bioconcentration factors up to 138 (Yang et al., 1999,
547 Xu et al. 2012). Qiang and Xiao-rong (1994) measured La concentrations in *Cyprinus carpio* after
548 5-45 days exposure at 0.5 mg L⁻¹ of lanthanum nitrate. They found bioconcentration factors up to 18
549 and 91, respectively, in gills and internal organs. Hao et al. (1996) evaluated the elimination period
550 of La from different parts of the body. They found two different forms of La: one, accounting for
551 50-70% of total La, unbound to tissues, which can be eliminated in short periods (< 1 day) and
552 another form tightly bound to tissues, which is eliminated after a longer time (half-lives up to 693
553 day in the skeleton). Landman et al. (2007) documented in a whole-lake LMB application a
554 significant La accumulation in fish liver and hepatopancreas, but low concentrations in the flesh
555 (cited in Hickey and Gibbs, 2009).

556

557 Table 2 - Summary of the most informative ecotoxicological thresholds estimated for Lanthanum
 558 Modified Bentonite (LMB) and Lanthanum. EC₅₀=50% Effect Concentration (mg L⁻¹); NOEC=No
 559 Effect Concentration (mg L⁻¹); LOEC= Lowest Observed Effect Concentration (mg L⁻¹)

Test organism	Test conditions	Stressor	Endpoint	EC ₅₀	NOEC	Reference
Zooplankton						
<i>Daphnia carinata</i>	LaCl ₃ , solution, soft water, 48 hours	FLa	Mortality	0.04		Barry and Meehan, 2000
<i>Daphnia carinata</i>	LaCl ₃ , solution, hard water, 48 hours	FLa	Mortality	1.18		Barry and Meehan, 2000
<i>Daphnia carinata</i>	LaCl ₃ , solution, hard water, 6 days	FLa	Survival, growth		<0,06	Barry and Meehan, 2000
<i>Daphnia magna</i>	not specified, solution, 48 hours	FLa	Reproduction	24		Sneller et al., 2000
<i>Daphnia magna</i>	La(NO ₃) ₃ •6H ₂ O, food suspension, P-containing medium, 14 days	FLa	Growth (length)		LOEC = 0,1	Lürling and Tolman, 2010
<i>Daphnia magna</i>	LaCl ₃ , solution, hard water, 21 days	FLa	Reproduction		0.1	Sneller et al., 2000
<i>Daphnia magna</i>	LMB, suspension, 5 days	LMB	Juvenile growth (weight)	871	100	Lürling and Tolman, 2010
<i>Daphnia magna</i>	LMB, suspension, 5 days	LMB	Juvenile growth (length)	1557	500	Lürling and Tolman, 2010
<i>Daphnia magna</i>	LMB, suspension, 48 hours	LMB	Immobilization	>50000		Martin and Hickey, 2004
<i>Daphnia magna</i>	LMB, suspension, 48 hours	LMB	Mortality	4900		Watson-Leung, 2008
<i>Ceriodaphnia dubia</i>	LaCl ₃ , solution, 48 hours	FLa	Immobilization	5	2.6	Stauber and Binet, 2000
<i>Ceriodaphnia dubia</i>	LaCl ₃ , solution, 7 days	FLa	Reproduction	0.43	0.05	Stauber and Binet, 2000
<i>Ceriodaphnia dubia</i>	LMB, Leachate, 48 hours	FLa	Mortality	0.08		Stauber, 2000
<i>Ceriodaphnia dubia</i>	LMB, Leachate, 7 days	FLa	Mortality	0.82		Stauber, 2000
<i>Ceriodaphnia dubia</i>	LMB, Leachate, 7 days	FLa	Reproduction	0.28		Stauber, 2000
<i>Ceriodaphnia dubia</i>	LMB, suspension, 48 hours	LMB	Immobilization	>50		ECOTOX, 2008
<i>Ceriodaphnia dubia</i>	LMB, suspension, 7 days	LMB	Immobilization and reproduction	>1		ECOTOX, 2008
<i>Brachionus calyciflorus</i>	LMB, suspension, 48 hours	LMB	Population growth rate	154	100	Van Oosterhout and Lürling, 2013
Fish						
<i>Melanotaenia duboulayi</i>	LaCl ₃ , solution, 96 hours	FLa	Immobilization	<0,6	<0,6	Stauber and Binet, 2000
<i>Oncorhynchus mykiss</i>	LMB, suspension, 48 hours	LMB	Mortality	>13600		Watson-Leung, 2008
Macroinvertebrates						
<i>Hyalella azteca</i>	LaCl ₃ , solution, soft water, 7 days	FLa	Mortality	0.02		Borgmann et al., 2005
<i>Hyalella azteca</i>	LaCl ₃ , solution, hard water, 7 days	FLa	Mortality	1,67 (nominal)		Borgmann et al., 2005
<i>Hyalella azteca</i>	LMB, suspension, 14 days	LMB	Survival and growth	>3400		Watson-Leung, 2008
<i>Hexagenia</i> sp.	LMB, suspension, 21 days	LMB	Survival and growth	>450		Watson-Leung, 2008
<i>Chironomus dilutus</i>	LMB, suspension, 38 days	LMB	Survival and growth	>450		Watson-Leung, 2008
<i>Chironomus zealandicus</i>	LMB, suspension, 38 days	LMB	Survival, emergence, sex ratio	>400	400	Clearwater, 2004
Nematodes						
<i>Caenorhabditis elegans</i>	LaCl ₃ , solution, 72 hours	FLa	Growth, reproduction		1.39	Zhang et al., 2010
Macrophytes						
<i>Hydrocharis dubia</i>	La(NO ₃) ₃ , solution, 7 days	FLa	Chlorophyll content	2.78		Xu et al., 2012
<i>Hydrilla verticillata</i>	La(NO ₃) ₃ , solution, 10 days	FLa	Chlorophyll content, oxidative stress		1.39	Wang et al., 2007

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568 4.2 *Human health implications of LMB use*

569 Regulatory bodies in Australia such as the NICNAS (National Industrial Chemical Notification and
570 Assessment Scheme) have considered LMB as a non-toxic product (NICNAS 2001). This initial
571 toxicity assessment of LMB was based on dissolved/bioavailable lanthanum in the water body after
572 a LMB application. Most of our knowledge on potential health effects of lanthanum carbonate
573 arises from the studies related to the use of the phosphate binding agent Fosrenol® (lanthanum
574 carbonate hydrate) used in patients with impaired renal function, in particular those undergoing
575 dialysis (Komaba et al., 2015; Hutchison et al., 2009; Behets et al., 2004a). Lanthanum carbonate
576 dissociates in the acid environment of the upper gastrointestinal tract to release lanthanum ions that
577 allow the formation of the insoluble lanthanum phosphate which is eliminated in the feces.
578 The oral bioavailability of lanthanum is low (< 0.001%) (Damment and Pennick 2008). The small
579 absorbed fraction is excreted predominantly in bile, with less than 2% being eliminated by the
580 kidneys (Pennick et al., 2006). With almost complete plasma protein binding, La^{+3} concentrations in
581 patients receiving doses up to 3 g day over several years at steady state are <3 ng L⁻¹ (Damment and
582 Pennick 2008). These properties greatly reduce systemic exposure, tissue deposition and the
583 potential for adverse effects.

584 Due to its affinity for phosphate, lanthanum is considered a bone-seeking element. Using
585 appropriate rat models of chronic kidney disease evidence was provided that lanthanum did not
586 exert a direct detrimental effect on bone (Behets et al., 2004b, Bervoets et al., 2006) and La did not
587 accumulate at critical sites of bone mineralization formation (Behets et al., 2005). On the contrary,
588 La was found to reduce the biochemical and mineral abnormalities in bone related to chronic kidney
589 disease (Damment et al., 2011). La carbonate-treated dialysis patients showed almost no evolution
590 toward low bone turnover nor did they experience any significant accumulation of La in bone or
591 blood or any aluminum-like effects on bone (D'Haese et al., 2003). Studies in rats and animals also
592 reported therapeutic use of lanthanum carbonate to reduce aortic calcifications (Neven et al., 2009;
593 Ohtake et al., 2013).

594 The liver is the main excretory organ of La. Within the liver, lanthanum has been observed in
595 lysosomes particularly in close proximity to and, also, within the bile canaliculi but not in or
596 attached to any other subcellular organelle (Bervoets et al., 2009). Lysosomes ultimately result in
597 the cellular release of La into bile (exocytosis). Clinical studies with up to 6 years of follow-up have
598 not disclosed any hepatotoxic effect of the drug in patients treated with this lanthanum carbonate
599 (Hutchison et al., 2009).

600 Although from an ultrastructural point of view one would not readily expect La to be able to
601 traverse the tight junctions in the blood-brain barrier, some concern has been raised about the
602 elements potential accumulation in this organ, thereby linking potential brain toxicity of La to the
603 neurological disorders reported with aluminum; i.e. dialysis dementia (Arieff 1985) and
604 Alzheimer's disease (Walton 2014). In studies to investigate possible neurotoxic effects of La
605 exposure, La was determined in several regions of the brain after administration of intravenous
606 doses (0.03–0.3 mg kg⁻¹ day⁻¹ over 4 weeks) and oral gavage (838-1500 mg kg⁻¹ day⁻¹). No La
607 could be detected (less than 6 ng g⁻¹), this despite the fact that in the rats having received La
608 intravenously, the median plasma La concentration was >300-fold higher than that seen in
609 experiments after oral loading (Persy et al., 2006; Damment et al., 2009). Evaluation of cognitive
610 function over a 2-year time period in patients on dialysis receiving lanthanum carbonate did not
611 reveal any additive effect of La upon deterioration inherent to aging and dialysis treatment
612 (Altmann et al., 2007). Nevertheless, based on data from experimental studies, Feng et al. (2006a
613 and b) and He et al. (2008) warned against the potential of neurotoxicity associated with La
614 exposure. Based on the results from these studies NICNAS assessed the risk related to the use of
615 LMB in a Secondary Notification report (NICNAS 2014). However, results of these studies should
616 be interpreted with caution, as no direct neurotoxicity end-point was evaluated and observed
617 changes in the parameters under study were rather marginal and/or a clear dose-response
618 relationship was lacking.

619 Exposure to La when used therapeutically is several orders of magnitude higher compared to the
620 concentrations humans are potentially exposed to via intake of water treated with LMB (i.e.
621 lanthanum carbonate daily dose 375-4500 mg). Indeed patients treated with lanthanum carbonate
622 for phosphate control receive daily doses varying between 375-4500 mg whilst, according to Spears
623 et al. (2013b), maximum FLa peak levels during and shortly after application of LMB lakes do not
624 exceed $0.414 \text{ mg La L}^{-1}$. Hence, in a worst case scenario assuming a daily water intake of 1.5 liter
625 day^{-1} exposure, this would correspond with a maximal intake of around $0.600 \text{ mg La day}^{-1}$; i.e. 625
626 times lower than the lowest dose used therapeutically. In an average application of LMB (such as
627 100 mg L^{-1}) the concentration of TLa would equate to 5 mg La L^{-1} . Assuming in a theoretical worst
628 case scenario that 100% of La (5% La content in the LMB) will be leached out of the product and
629 will not bind phosphate or other compounds, then a person would need to drink 300 L of the treated
630 water per day to ingest the minimum dose of La that corresponds to the lowest lanthanum carbonate
631 (Fosrenol®) daily intake. To reduce plasma phosphate levels to less than 6.0 mg dL^{-1} in uremic
632 patients, normally the maximum daily dose of Fosrenol® required is 3000 mg and therefore the
633 average person would need to drink 1200 L of treated water per day to ingest the maximum dose of
634 La that is the Fosrenol® daily intake. Moreover, there is no reason to believe that La taken up via
635 the drinking water would not bind phosphate in the gut and form an insoluble complex that will be
636 eliminated via the feces. Hence, gastrointestinal absorption through exposure via drinking water as
637 well as tissue accumulation will be extremely low posing no increased risk for possible health
638 effects.

639 In a fish health monitoring report conducted in Lake Okareka (New Zealand) Landman et al. (2007)
640 demonstrated that rainbow trout (*Oncorhynchus mykiss*) and koura (*Paranephrops planifrons*)
641 accumulated La in the liver and hepatopancreas tissue, not in the flesh/muscle following the
642 application of LMB. It was also demonstrated that La was removed from the fish liver and
643 hepatopancreas tissues within a few months, suggesting a biological capacity of the fish to deplete
644 La. This is in line with Bervoets et al (2009) who demonstrated the hepatobiliary excretion of La in

645 rat studies. The highest total concentration of La measured in the liver and hepatopancreas tissue of
646 trout in Lake Okareka after one and two months of LMB application was 1.2 and 0.8 mg kg⁻¹ and
647 the highest concentration of La in the hepatopancreas tissues of male and female trout was 0.8 and
648 1.0 mg kg⁻¹, respectively (Landman et al., 2007). Therefore, in total the highest concentration of La
649 in one trout was 2.0 mg kg⁻¹. Thus, a person would need to consume 187.5 kg of fish per day to
650 ingest the minimum daily dose of lanthanum carbonate (Fosrenol®). Referring to the recommended
651 maximum dosage of lanthanum carbonate an average person would need to consume 1500 kg of
652 fish per day to consume the maximum dose of 3000 mg d⁻¹. Considering that liver and
653 hepatopancreas normally will not be eaten by humans, the risk to human health from consumption
654 of fish harvested from a LMB treated water body is negligible.

655

656 5. Discussion

657 The results of the LMB application presented in this review underline a strong efficiency of this
658 product in reducing the SRP concentrations in the water column and the P flux from sediments.
659 This efficiency has been confirmed in laboratory, mesocosm and field trials. However, in the
660 presence of high DOC concentrations SRP removal can be limited (Douglas, 2000; Lürling et al.,
661 2014; Dithmer et al., this Issue) or even absent (Geurts et al., 2011). Also the interference with
662 oxyanions other than PO₄ was highlighted as a confounding factor (e.g. Reitzel et al., 2013a).
663 However, in a recent study Dithmer et al. (this issue) did not find any correlation between alkalinity
664 and P binding capacity of the LMB. Apart from these limitations the LMB efficiently binds SRP in
665 fresh water ecosystems and over a wide range of physico-chemical conditions, with particular
666 respect to pH. Maximum efficiency in P binding has been found in a 5-7 pH range, while the
667 efficiency decreases markedly at pH higher than 9. Such high pH values are generally indicative of
668 strong photosynthetic activity (potentially due to both macrophytes and phytoplankton) in eutrophic
669 lakes. Under these conditions (and in particular during algal blooms) the sole LMB application is
670 not recommended, because of the commonly observed high pH and low SRP concentrations,

671 making timing a crucial component of the application. Usually winter in temperate regions will
672 offer the best window of opportunity with probably least side effects on biota. Also the use of this
673 product in saline environments, cannot be a priori recommended due to potential lanthanum release
674 as underlined by pre-commercialization studies (Douglas personal communication). In this way it
675 has to be underlined that data on the LMB behavior in saline or brackish waters are scarce. In one
676 of the few studies available, however, Reitzel et al. (2013a) found only a slight increase ($< 1\%$) of
677 filtered TLa ($La < 0.2\ \mu\text{m}$), a 5% increase of unfiltered TLa ($La > 0.2\ \mu\text{m}$) and 9% of TLa adhering
678 to the walls of the plastic tubes used in their tests in moderately saline water (15 ppt). These results
679 indicate leakage of La from the clay matrix in moderate salinity water of about 15% . At the
680 moment the application of this product in even moderately saline environments need a careful risk
681 and case by case evaluation. The results presented in this review allow to generalize this concept
682 and to highlight the importance of carefully plan any field application and trial. In this way the
683 results of the Deep Creek Reservoir are emblematic (NICNAS, 2014). A LMB trial was conducted
684 in Deep Creek Reservoir, Australia in 2007 (Chapman et al., 2009, NICNAS, 2014). In this trial an
685 approximately three times overdosing of LMB based on FRP concentrations occurred with a
686 resultant maximum concentration of dissolved La of $220\ \mu\text{g L}^{-1}$. Addition also occurred of other
687 non-LMB agents that may have compromised the trial integrity. Temporally-associated fish
688 mortalities occurred for up to two weeks post reagent application (NICNAS, 2014). Few living
689 zooplankton individuals were identified in the reservoir seven weeks post-LMB application
690 (NICNAS, 2014) with a possible link postulated between the LMB application and lethal effects on
691 aquatic biota from two trophic levels.

692 Based on all available medical information, LMB can safely be applied in bathing water and
693 drinking water reservoirs as long as these are not soft or acidic water bodies. From an
694 ecotoxicological perspective, most studies indicate toxicity thresholds above the LMB and FLa
695 concentrations reported after field scale applications (see sections 3.3 and 4.5 in this paper).
696 Nonetheless, concentrations during and shortly after application may be closer or higher than the

697 estimated ecotoxicological thresholds, in particular for zooplankton species (*Brachionus*
698 *calyciflorus*, *Daphnia magna* and *Ceriodaphnia dubia*), which proved to be the most sensitive
699 among the organisms tested (Table 2).

700 Effects on benthic invertebrates, which are directly exposed to LMB through ingestion, need to be
701 further explored. Potentially, the risk of La^{3+} persistence appears to increase under low alkalinity
702 and low DOC concentrations and this should be considered further. Indeed, the presence of P or
703 other ligands (e.g. HCO_3^- , humic acids, OH^- , etc.) in the water is an important factor when assessing
704 the toxicity of lanthanum, altering the bioavailability of the metal. No obvious ecotoxicological
705 effects were reported in field scale trials, although it should be noted that these effects are
706 particularly difficult to quantify, comprehensively, at the whole lake scale. It should be considered
707 that LMB is generally applied in lakes with high trophic state, where the presence of phosphorous
708 or other ligands may reduce the bioavailability of FLA and other impurities, resulting in reduced
709 toxicity potential.

710 Effects of LMB application could be related to food reduction and/or to high turbidity (i.e. physical
711 effect). For what concerns laboratory tests with zooplankton organisms, the reduction of algae after
712 a LMB application was proved to cause a reduction on growth, as effects of starving (Van
713 Oosterhout and Lürling, 2011). Besides, the increased turbidity could also result in a reduced
714 grazing activity for zooplankton or in clogging of feeding or respiration structures for invertebrates
715 and fish (e.g. Kirk, 1991). For these reasons, the potential effects of LMB applications in natural
716 waters at higher levels of biological organization (i.e. community, ecosystems) needs to be further
717 explored with long-term monitoring.

718 Another concern is bioaccumulation of La in aquatic organisms, which was evaluated in
719 crustaceans, macrophytes and fish. Bioconcentration factors up to 91 were found in the internal
720 organs of fish (Qiang and Xiao-rong, 1994), but further experiments proved that most La
721 accumulated can be eliminated in short periods (Hao et al., 1996; Landman et al., 2007). Longer

722 elimination times are needed for La accumulated in internal organs and skeletons. For this reason,
723 potential toxicity at higher trophic levels (e.g. apex predators) should be evaluated.

724 The scarcity of long term studies, extending far beyond the estimated recovery times of lanthanum
725 concentrations comparable to baseline levels is evident (Spears et al., 2013b). This indicates that
726 potential long term impacts derived from LMB application have, so far, been largely unexplored,
727 but see for instance Waajen et al. (this issue). There are several cases that have been monitored up
728 to 7 years after LMB addition, without any signs of ecosystem or community level deterioration. In
729 contrast, eutrophic lakes like Rauwbraken and De Kuil showed strong expansion of submerged
730 macrophytes, improving ecological structure and promoting macrofauna, zooplankton and fish
731 abundance (Waajen et al., this issue). As such, these systems show clear signs of ecological
732 recovery in line with longer-term eutrophication control studies in which catchment P loading has
733 been reduced (Jeppesen et al., 2005).

734 In general, ecological recovery following eutrophication control has been well described in the
735 literature (Brooks et al., 2001; Jeppesen et al., 2005; Rossaro et al., 2011; Verdonschot et al., 2013).
736 A minimum of a few to some tens of years for recovery were indicated overall (Jeppesen et al.,
737 2005; Verdonschot et al., 2013). Nevertheless, the number of studied cases showing recovery times
738 of trophic status as fast as those typically observed in the case of LMB applications is minimal.

739 Consequently, any robust comparison of biological responses is difficult, and forecasting the
740 ecological responses after LMB applications remains challenging, as exemplified by the studies of
741 Novak and Chambers (2014) and Gunn et al. (2014). Moreover, other confounding drivers, such as
742 climatic perturbations (Moos et al., 2014) or the competition by exotic species (Gunn et al., 2014)
743 may hamper the recovery of acceptable communities. The potential confounding effects of invasive
744 species on ecological restoration is a remarkable question in freshwater ecology (van der Wal et al.,
745 2013; Pires et al., 2007; Villeger et al., 2014).

746 Furthermore, the sudden trophic reduction (e.g. food availability) caused by geoengineering
747 techniques may lead to the temporal disappearance of taxa, such as large bodied cladocera or

748 juvenile fish (Van Oosterhout and Lüring, 2011). However, as evidenced from the shock therapies
749 in Lake Rauwbraken and Lake De Kuil, the resilience of ecosystems may often compensate for
750 these perturbations.

751 It is noteworthy that forecasting the lake responses after LMB applications is crucial, for instance,
752 in a policy perspective, since achieving pre-defined “good ecological status” is warranted by the
753 parallel restoration of ‘reference’ or ‘unimpacted’ communities for many groups, such as
754 phytoplankton, fish or macrophytes (i.e. in the case of the EU Water Framework Directive).

755 From a management point of view, the restoration of ecosystem services is crucial where the
756 ecological status reflects the conditions to fulfil these services. An evaluation of risks derived by the
757 application of LMB may benefit from preliminary biodiversity surveys aimed at evaluating the
758 presence of key or conservation relevant species, as well as exotic species. Similarly, the use of
759 predictive tools, such as ecological trophic models, or retrospective paleoecological approaches
760 may help to evaluate the uncertainties associated with restoration goals. In conclusions, the
761 possibility of a long recovery period (Hickey and Gibbs, 2009; Zamparas and Zacharias, 2014), as
762 already demonstrated in many lakes after external P loadings control (Romo et al., 2005; Villena
763 and Romo, 2003), should be taken into account in a risk assessment evaluation. Particularly, doing
764 nothing and therewith taking prolonged toxic cyanobacteria blooms for granted should be assessed
765 against the potential positive and negative impacts of any management measure, including the use
766 of LMB. This review will hopefully provide the evidence necessary to support such assessments.

767 In general terms, however, it can be argued that due to the multiplicity of environmental factors
768 involved, the efficiency and the risk related to the application of the LMB are inevitably site-
769 specific and the risks, in particular, can be minimized adopting specific measures accounting for the
770 site specific variations (e.g. NICNAS, 2001).

771 Cost may be a factor when considering using LMB in lake restoration. The price of lanthanum is of the
772 order of thousands of dollars per ton, that is, for instance, around one order of magnitude higher
773 than the cost of aluminum. The data presented in this paper, however, underline that LMB

774 phosphorus fixation (unlike the aluminum-mediated fixation) is highly stable under a wide range of
775 physico-chemical conditions. Both techniques should be therefore considered as a tool available to
776 the lake manager, whose use depends on site-specific circumstances definable only through a
777 thorough system analysis.

778

779 **6. Conclusions**

- 780 • The majority of the data related to the efficiency of LMB indicated effective reduction of
781 SRP concentrations in the water column and control of sediment SRP release, under most
782 environmental conditions, and across laboratory, mesocosm and field scale trials in
783 freshwater ecosystems.
- 784 • The operational performance of LMB is reduced in the presence of humic substances and in
785 the presence of competing oxyanions in addition to PO₄.
- 786 • the sole LMB application during strong photosynthetic activity (e.g. during algal blooms) is
787 not recommended, due to the generally observed high pH and low SRP concentrations.
- 788 • The use of LMB in low alkalinity waters is not advised without thorough pretreatment testing
789 to ensure that free La is not present in the water.
- 790 • The use of LMB in saline environments is not *a priori* recommended.
- 791 • La concentrations detected during or immediately after a LMB application are generally
792 below acute toxicological threshold of different organisms, with the exception of
793 zooplankton species (e.g. *Daphnia magna* and *Ceriodaphnia dubia*), however, short term
794 negative effects of suspended solids should be further examined.
- 795 • The human health risks associated with LMB treated surface waters appear to be negligible;
- 796 • There are no published examples of long-term negative ecotoxicological effects in LMB
797 treated ecosystems. However, observed La uptake by organisms warrants longer-term
798 investigation, especially at the field scale and particularly for sediment dwelling organisms.

799

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803

804

ACCEPTED MANUSCRIPT

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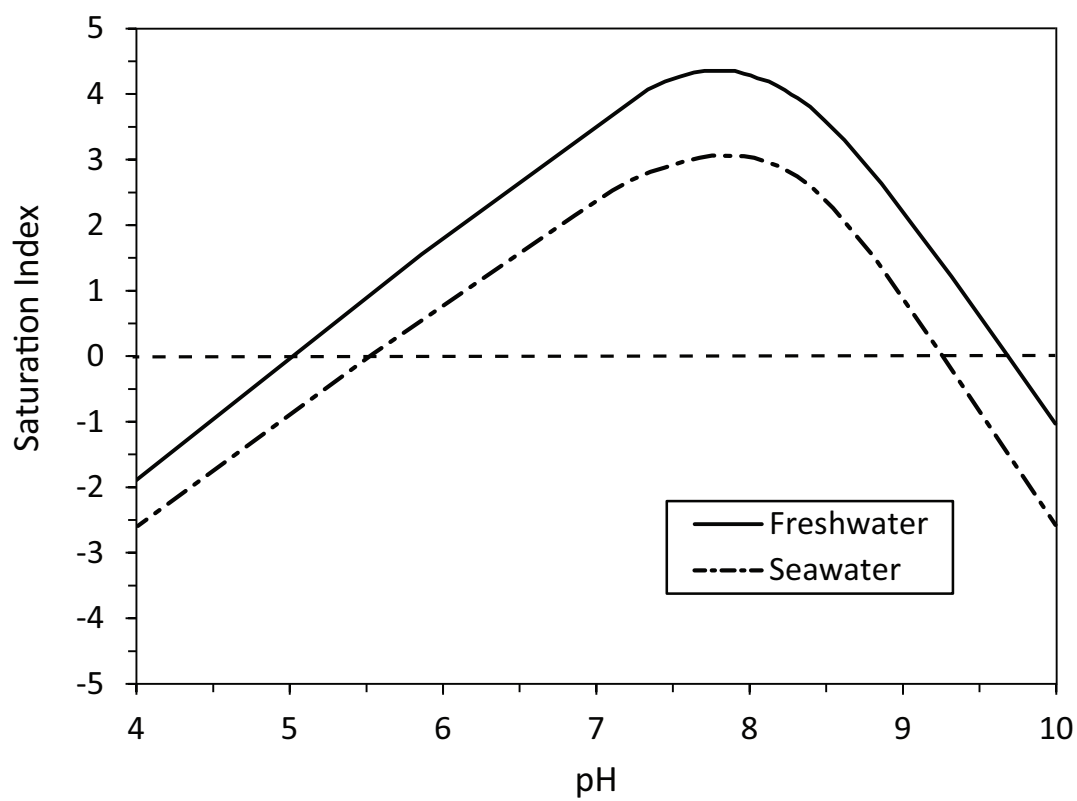
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High phosphorus binding efficiency of the lanthanum modified bentonite

Efficiency is reduced by the presence of humic substances and competing oxyanions

Low eco-toxicological and human health risks

Long term investigation are suggested to verify the impact on the ecosystem

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