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

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Abstract

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

Keywords: lanthanum modified bentonite; toxicity; phosphorus; sediments; ecological recovery; geo-engineering
1. Introduction

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

To address this we draw on the experiences of a wide range of research groups who have led the development and assessment of LMB for use as a eutrophication management tool to review the collective evidence base. This paper addresses the following overarching questions: what was the general scientific premise underpinning the development of LMB; what evidence is available at laboratory, mesocosm, and field scales to support the use of LMB in lakes; and what are the
positive and negative environmental and human health implications of its use? We address these questions by drawing on evidence from (up to March 2015) 40 peer reviewed publications and 10 technical reports. Three relevant papers published in this special issue were also taken into account.

2. Early development of LMB

LMB was borne from a need to develop a P (more specifically, phosphate $\text{PO}_4^{3-}$) absorbent for application to eutrophic systems that could be easily applied and was environmentally compatible in terms of its physico-chemical characteristics and ecotoxicological profile. LMB was extensively evaluated at laboratory, pilot and field scale prior to patenting and commercialization by CSIRO. In documenting the research and development of the LMB, a range of aspects including the geochemistry of lanthanides, more commonly known as the rare earth elements (REEs), their commercial sources, laboratory and field trials of the LMB and patenting commercial aspects are discussed below.

2.1 Lanthanum and other rare earth elements in the biosphere

Within the biosphere, few elements are known to bind strongly to $\text{PO}_4^{3-}$ to form minerals that are stable over a range of pH and redox conditions commonly encountered in natural waters. The REEs form a coherent chemical series from the atomic number $Z=57$ to 71 but which also include yttrium [Y] and scandium [Sc]. The majority of REEs are trivalent, however both cerium [Ce; +4, +3] and europium [Eu; +2, +3] may have different redox-sensitive oxidation states. In general, the REEs behave geochemically as a coherent group, however, the well-known lanthanide contraction (that leads to a decline in ionic radius from 1.13 Å for $\text{La}^{3+}$ to 1.00 Å for $\text{Lu}^{3+}$) confers a subtle change in properties, notwithstanding the alternative Ce and Eu oxidation states. Within the group the light REEs such as lanthanum [La] are by far the most abundant. By way of comparison La ($38 \mu g \text{ g}^{-1}$) and Ce ($80 \mu g \text{ g}^{-1}$) are similar to elements such as copper [Cu; $50 \mu g \text{ g}^{-1}$] and other elements like cobalt [Co; $23 \mu g \text{ g}^{-1}$], and lead [Pb; $20 \mu g \text{ g}^{-1}$] in terms of average crustal abundance (Taylor and
McLennan, 1985). The light REEs also have a substantially greater natural abundance relative to the heavy REEs such as ytterbium \([\text{Yb}; 2.8 \, \mu\text{g} \, \text{g}^{-1}]\). Within the biosphere, the REEs may also be found in a range of rocks, sediments (e.g. Moermond et al., 2001) and soils (Tyler, 2004) as well as in terrestrial (Markert, 1987) and aquatic biota (Ure and Bacon, 1978; Mayfield and Fairbrother, 2015).

Sources of REEs are generally confined to two types, that of heavy mineral-enriched beach sands, or primary or secondary igneous pegmatite-hosted deposits. While the environmental persistence of the REE-PO$_4$ minerals can be considered a virtue, the often closed systems allow accumulation of daughter radionuclides, often without net loss leading to a substantial activity, particularly when the minerals are concentrated. In addition, separation of the radionuclides may be incomplete leading to low levels of residual radioactivity associated with the REE. In the specific context of environmental applications, this factor may reduce their range of practical uses. This challenge, however, has largely been overcome due to the existence of the large REE deposit in Baotou, located in Inner Mongolia which has been estimated to host approximately 75% of the world’s known REE reserves (Zhongxin et al., 1992). This deposit and the LaCl$_3$ produced from it is of inherently low radioactivity compared to many heavy mineral-hosted REE deposits such that it is often lower than that of many of the soils and bottom sediments at the sites where it is utilized.

2.2 The development of lanthanum modified bentonite (LMB)

There is a naturally strong affinity of La and other REEs with PO$_4$. Based on its abundance and single oxidation state, La, was chosen as the most prospective REE to use to explore possible application in the binding of PO$_4$ in aquatic environments to replicate one or more of the minerals commonly found in the natural environment. While a robust bond could be formed between La and PO$_4$, another key factor was the simple 1:1 stoichiometry without the requirement for other moieties or intermediates, thus simplifying potential real world applications. Earlier research had also suggested a potential for the use of La for the removal of PO$_4$ from wastewaters (e.g. Melnyk et al.,
A major factor that was considered during the development of this P binding product was the search for a suitable carrier-exchange system that could contain a reservoir of La available for the complexation with PO$_4$. This would negate the inherent toxicity associated with the dissolved (“free”) La (e.g. Barry and Meehan, 2000; Oral et al., 2010) and mitigate the dilution or advection in the site of application. To this end, and after considerable testing with a range of minerals, a bentonite was chosen as the carrier exchange substrate (Douglas et al., 2000). Advantageously, the bentonite also satisfied a number of other requirements. Being an aluminosilicate mineral, it was considered compatible with application to clay-rich aquatic suspended and bottom sediments. Having similar density and particles size, upon settling it could be incorporated as a seamless component of the bottom sediment thus limiting physical resuspension or bioturbation. Furthermore, the bentonite has an inherently low toxicity, is commercially available in large quantities around the world and typically possesses a moderate to high cation exchange capacity (CEC) of between 60 and 100 meq 100 g$^{-1}$. Correctly prepared, a typical LMB has a La concentration of ca. 5% depending on the precursor bentonite CEC, a concomitant PO$_4$-P-uptake capacity of ca. 1%, and a low residual La concentration within the co-existing solute (Douglas et al., 2000).

2.3 Preliminary laboratory and pilot-scale field trials

Initial laboratory trials using LMB in batch mode, aquatic sediment core incubations and within small (1m diameter) and large (6m diameter) mesocosms confirmed the efficacy of the LMB as an efficient PO$_4$ sorbent able to reduce the dissolved P load in the water column and the internal P loading by reducing the sediment-derived PO$_4$ fluxes (Douglas et al., 1999). In particular, the efficiency of the LMB in P-binding was tested on a range of sediment cores and surface waters and on wastewater samples. Soluble reactive phosphorus (SRP) concentrations (initial range 120-130 µg P L$^{-1}$) in pore water sediment cores were reduced by more than 98% in a 7 day batch-test and by 87-98% in a 48 hours batch test conducted on surface water samples (initial SRP concentration range
20-450 µg P L\(^{-1}\)). Batch tests on wastewaters with SRP initial concentrations of 1,130 to 5,320 µg P L\(^{-1}\) demonstrated removal percentages of greater than 99%.

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

Initial mineralogical characterization of the reaction products produced by the LMB in contact with PO\(_4\) solutions indicated the formation of rhabdophane, a hydrated mineral of the formula LaPO\(_4\)·nH\(_2\)O commonly found as a weathering product of REE-PO\(_4\) minerals (e.g. Jonasson et al., 1988). This confirmed the efficient 1:1 La to PO\(_4\) binding stoichiometry and the production of a mineral known to be stable across a range wide range of terrestrial and aquatic environments (e.g. Nagy and Draganits, 1999).

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

During laboratory-scale evaluation it was found that substantial La may be released from LMB if exposed to saline environments (Douglas et al., 2000). This has two effects. In the short-term, the first is to introduce a range of soluble La species into the water column with the likelihood of significant ecotoxicological effects. The second medium to long-term effect, due to partial or complete La loss, is to substantially reduce efficacy or render the LMB ineffective respectively as a reactive layer for the absorption of labile P species at the sediment-water interface.
The results of this experimentation indicated that the application of the LMB in even moderately saline environments of >0.5 ppt is to be avoided (Douglas personal communication).

A large-scale pre-commercial application of LMB was undertaken in the Canning River in metropolitan Perth, Western Australia in early 2000 (Robb et al., 2003). This trial was conducted on a scale commensurate with that required for the management of P in eutrophic aquatic systems and demonstrated the efficacy of the LMB in reducing both initial water column SRP concentrations and internal sediment-derived loading. The Australian and international patents were lodged and a commercial partner to exploit the intellectual property developed by CSIRO, was identified and engaged.

Figure 1. Modelled Saturation Index (SI) for the formation of rhabdophane (LaPO₄.nH₂O) in freshwater and seawater between pH 4 and 10.
3. Evidence of LMB use for the control of P in lakes leading to ecological recovery

3.1 LMB laboratory studies - P binding efficiency and confounding factors

Solid state $^{31}$P NMR studies of the binding between phosphate and La, have shown that rhabdophane (LaPO$_4$·H$_2$O) is formed initially after adding the LMB to the water. In addition to that directly bound within the rhabdophane-(La), around 20% of the SRP bound by the LMB can be found as adsorbed onto the rhabdophane surface (Dithmer et al. 2015). However, aging of the rhabdophane may lead to the formation of monazite (LaPO$_4$) which has an even lower solubility than rhabdophane (Cetiner et al., 2005; Dithmer et al., 2015). The behaviour of the lanthanum phosphate minerals is thus markedly different from that of aluminium hydroxides, which may lose more than 50% of their initial P binding capacity upon aging (e.g. Berkowitz et al., 2006).

Several studies have indicated La:SRP binding ratios above the expected stoichiometric ratio of 1:1, suggesting interference in the rhabdophane formation. Using waters from Danish lakes Reitzel et al. (2013a) found that the LMB performed better in soft waters compared to hard waters and concluded that carbonate was probably competing with phosphate for binding onto La (Johannesson et al., 1995). However, a recent study performed in lake and pore water from 16 Danish lakes with varying alkalinities, did not show any correlation between alkalinity and P binding capacity of the LMB (Dithmer et al., this Issue). Instead, a significant negative correlation was found between lake water DOC concentrations and SRP binding capacity of the LMB, demonstrating that DOC interferes with the rhabdophane formation. This result supports the findings by different authors (e.g. Douglas, 2000 and Lürling et al., 2014) who observed constrained P removal by LMB in soils and waters rich in DOC. In particular, Lürling et al., 2014 conducted laboratory controlled experiments where the efficiency of the LMB was verified in the presence and in the absence of humic substances. The authors found that in both short (1 day) and long term (42 day) experiments the efficiency of LMB was reduced in the presence of humic substances. In the presence of 10 mg
L$^{-1}$ DOC the authors also found a strong increase of filterable La that in a week reached values higher than 270 µg La L$^{-1}$. However, recent findings have demonstrated that given enough time SRP will eventually be bound to the La, thereby overcoming the interference by DOC (Dithmer et al., this issue).

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

Laboratory investigations on the effect of pH on the binding of PO$_4^{3-}$ by LMB indicated maximum efficiency in a pH range of 5-7 with absorption capacity decreasing at pH higher than 9 (Figure 1 and Ross et al., 2008; Haghseresht et al. 2009). The greatest affinity was found for the H$_2$PO$_4^{1-}$ monovalent phosphate ion. Similar results were found by Zamparas et al. (2012) who compared the P-binding efficiency of the LMB with that of an unmodified bentonite (Zenith-N) and iron modified bentonite (Zenith-Fe). The authors indicated maximum P-binding efficiency in a 6-7 pH range.

Both modified bentonites showed less pH-dependence than the natural bentonite. Reitzel et al. (2013a), showed that increasing the pH to 9 reduced the formation of rhabdophane, compared to an experiment conducted at pH 7 because of increased hydroxylation of the La at pH 9 (Haghseresht et al., 2009). However, exposing P-saturated LMB to pH 9 did not lead to a significant release of P, confirming rhabdophane stability. This has important implications for the use of the LMB since it will be possible to dose the LMB to high pH (>9) waters, as long as the sediment pH is around neutral.

In relation to the P binding efficiency of LMB in bed sediments, Reitzel et al. (2013b) performed a 35 day incubation experiment using sediment cores from a Danish eutrophic lake. A sequential
extraction of P and La conducted after the incubation period underlined a reduction of the iron-bound P concentrations and an increase in the HCl-exchangeable P concentrations in the sediments treated with the LMB. Most of the La was found in the HCl extract or the residual extract indicating that P remained strongly bounded to La in the LMB matrix. In laboratory experiments Gibbs et al. (2011) found a small increase of filterable aluminum (Al) associated with the use of four different capping agents. The authors interpret that these variable Al concentrations may have been generated by ebullition through the capping layer within the incubation chambers. Further, an enhancement of ammonium release under aerobic conditions in the LMB treated incubation chambers was measured. Gibbs et al. (2011) attribute this to an effect on the nitrification process, but, as ebullition probably occurred, the higher ammonium concentrations could also partly derived from entrainment of pore water by ebullition.

3.2 LMB mesocosm trials - evidence of P control

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

In Lake Varese (Crosa et al., 2013) monthly sampling documented a substantial reduction the P concentration in the water column after the LMB application. Mean annual concentrations of total phosphorus (TP) and soluble reactive phosphorus (SRP) in the bottom water of the treated 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 P L\(^{-1}\), respectively. Moreover, at the end of the 11 months monitoring period TP and SRP
concentrations in the bottom water of the treated mesocosm were significantly lower compared to the untreated site, showing a reduction of more than 80% of the TP and SRP concentrations in the water column after the LMB application. The La\(^{3+}\) concentrations were below 5 µg L\(^{-1}\) one month after the application. Similar results were obtained by Márquez-Pacheco et al. (2013) who observed a 75% reduction of SRP concentrations in the water column applying a dose of LMB/TP of 40:1 within 18 days after the application. A 100:1 dose rate was sufficient to control SRP release from the sediment during the whole monitoring period of 42 days, whereas a dose of 15:1 was sufficient to reduce SRP concentrations by 25-50% for up to 15 days. In line with these results, Douglas et al. (1999) observed a rapid reduction of water column SRP concentrations, reaching 5 µg P L\(^{-1}\) within the first 24 hours after the application of the LMB. In the treated mesocosm the reduction of the SRP concentration was sustained for up to 73 days, whereas SRP concentrations in the control mesocosm exceeded 3.5 mg P L\(^{-1}\) by day 73. The reduction of SRP and TP during the monitoring period reached 94-100% and 83-96%, respectively. Different results are presented by Lürling and Faasen (2012) for a trial in a small urban pond. Over the whole monitoring period of 58 days, median TP and SRP concentrations in the LMB treated mesocosms were 0.58 mg P L\(^{-1}\) and 0.095 mg P L\(^{-1}\), respectively and did not differ substantially from the control sites (median TP 0.69 mg P L\(^{-1}\) and P 0.09 mg SRP L\(^{-1}\)). It was surmised that the P absorption capacity of LMB in this study could have been impaired by environmental factors such as pH and interference of humic acids.

3.3 LMB field trials

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

The first full scale application was conducted by Robb et al. (2003) in two impounded river sections in Western Australia (Canning and Vasse Rivers). The authors founds a marked reduction of SRP concentrations in the treated areas compared to untreated areas, in both systems. For the Canning River the mean summer TP concentrations dropped by 45% with the LMB treatment. A higher reduction (59%) was observed in the Vasse River by the summer application.
Similar results were recorded during a restoration project in Lake Rauwbraken, The Netherlands, using a combination of LMB and a low dose flocculent (Van Oosterhout and Lürling, 2011). The treatment reduced the TP concentrations in the water column more than 90% for up to 5 years (Lürling and van Oosterhout, 2013a).

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

Very high removal efficiency (80-95%) of TP and SRP within 2 weeks after LMB treatment were reported by Bishop et al. (2014) for the Laguna Niguel Lake, California, USA. Haghseresht et al. (2009) reported a TP and SRP reduction ranging from 85 to 99% in a Nursery Dam (Australia). Liu et al. (2009) in Lake Dianchi (China) reported a rapid decline in TP and SRP concentrations falling below the detection limit. Finally, in a pilot treatment of the LMB conducted in the artificial river ALA (China) Liu et al. (2012) reported a removal rate of the SRP about 97%.

A decrease in annual mean TP concentrations (about 50%) was also shown for lowland, high alkalinity and eutrophic Loch Flemington, Scotland, (Gunn et al., 2014) by the application of LMB. Spears et al. (this issue) assessed the responses in TP and SRP across multiple treated lakes (15 for TP and 14 for SRP) in the 24 months following LMB applications. TP concentrations across the lakes decreased markedly from a median of 0.08 mg P L⁻¹ in the 24 months pre-application to 0.03
mg P L\(^{-1}\) in the 24 months after the post-application. TP concentration reduction was most evident 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\(^{-1}\)). Decreases in SRP concentrations from 0.019 mg P L\(^{-1}\) to 0.005 mg P L\(^{-1}\) were reported at an annual frequency with the strong responses being reported in summer (0.018 mg P L\(^{-1}\) to 0.004 mg P L\(^{-1}\)), 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\(^{-1}\)).
Table 1. Summary of data reported for the aquatic systems cited in the review. SA = surface area, MD = max. depth, AD = average depth, WV = water volume, LMB = lanthanum modified bentonite, PAC = polyaluminium chloride

<table>
<thead>
<tr>
<th>Name</th>
<th>Country</th>
<th>Waterbody</th>
<th>Morphometry</th>
<th>Year of application</th>
<th>LMB (t)</th>
<th>LMB (kg m⁻²)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Laguna Niguel Lake</td>
<td>USA</td>
<td>Reservoir</td>
<td>SA=0.124 km²; MD=9.5 m; AD=3.7 m</td>
<td>2013</td>
<td>51.34</td>
<td>0.414</td>
<td>Bishop et al., 2014</td>
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<td>Cane Parkway</td>
<td>Canada</td>
<td>Stormwater pond</td>
<td>SA=0.0043 km²; AD=2 m</td>
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<td>-</td>
<td>-</td>
<td>Moos et al., 2014</td>
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<tr>
<td>Scanlon Creek Reservoir</td>
<td>Canada</td>
<td>Reservoir</td>
<td>SA=0.034 km²; AD=7 m</td>
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<td>0.53</td>
<td>Moos et al. 2014</td>
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<td>China</td>
<td>Trial pond</td>
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<td>2006</td>
<td>10</td>
<td>5</td>
<td>Liu et al. 2009,</td>
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<td>0.5</td>
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<td>Impoundet river section</td>
<td>MD&lt;3 m</td>
<td>2001/2002</td>
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<td>-</td>
<td>Robb et al., 2003; Novak and Chambers, 2014</td>
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<td>-</td>
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<td>20</td>
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<td>18 t LMB</td>
<td>0.45 LMB</td>
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<td>Sand excavation lake</td>
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<td>0.05 PAC</td>
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<td>25</td>
<td>0.159</td>
<td>Meis et al., 2013; Gunn et al., 2014</td>
</tr>
<tr>
<td>Clatto Reservoir</td>
<td>UK</td>
<td>Reservoir</td>
<td>SA=0.09 km²; AD=2.8 m</td>
<td>2009</td>
<td>24</td>
<td>0.267</td>
<td>Meis et al. 2012</td>
</tr>
</tbody>
</table>

3.3.2 LMB field trials – impacts on sediment P properties

The efficiency of the LMB in P binding in sediments has been evaluated in a number of studies. In laboratory and field experiments Liu et al., 2012 investigated the different P forms present in sediments and analysed their contributions to the P loadings of the artificial river ALA (China). A pilot project was pursued with the dose rate of LMB at 0.5 kg m⁻², in a section of the artificial river, with successive applications every three months, with a P-inactivation rate of the bed sediments reaching 31% after 1 year. Similar results were reported by Meis et al. (2012) in Clatto Reservoir, Scotland. 28 days following an application of LMB a significant increase of sediment La concentration in the upper 8 cm was found, indicating that LMB was transported deeper in the
sediment and a significant increase in the ‘residual P’ fraction in the top 2 cm of sediment was reported. Other sediment P-fractions, including $P_{\text{mobile}}$, did not differ significantly. Sequential extraction of P from saturated sediments by LMB under laboratory conditions indicated that around 21% of P bound by LMB was release-sensitive, while the remaining 79% was unlikely to be released even under reducing conditions in shallow lakes.

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

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

In Loch Flemington, monthly monitoring of the phytoplankton community was conducted 10 months before and 20 months after a 170 g m$^{-2}$ LMB application (Meis, 2012). Phytoplankton biomass decreased significantly the first season after the treatment, in correlation with P
concentration. On the contrary, changes in relative class abundances were found from the second season, and indicated a decrease of Cyanophyceae and an increase of Dinophyceae and Chlorophyceae.

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

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

In Lake Rauwbraken a marked reduction (5 times) of the Chl-a concentrations was detected and the lake shifted from an eutrophic-hypertrophic to an oligo-mesotrophic condition. A surface scum of *Aphanizomenon flos-aquae* present in the south-western part of the lake was successfully precipitated and a deep water abundant *Planktothrix rubescens* assemblage was removed. The study also evaluated the effect of the treatment on *Daphnia galeata*. In this lake a long term post-
treatment monitoring has been conducted between 2008 and 2014 and allowed to verify the stability of the achieved oligo-mesotrophic condition (Lürling unpublished data).

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

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

Novak and Chambers (2014) investigated the responses of macrophyte communities in two south-western Australian impounded rivers. In the Canning River (50 µg TP L\(^{-1}\)) since 2005 a near permanent switch to macrophyte dominance occurred, but a long recovery trajectory (about six years) and a significant external intervention, namely water level manipulation, where required to favour the onset of a stable macrophyte coverage. In the Vasse River no submerged macrophytes were observed in the years between 1996-2007, due to the persistence of a high trophic condition (150 µg TP L\(^{-1}\)) and to the pre-treatment absence of potential macrophyte colonizers. This study
supported thresholds of 150 µg TP L\(^{-1}\) indicating a high risk of macrophyte loss, 100 µg TP L\(^{-1}\) for maintenance of existing macrophyte beds, and lower than 100 µg TP L\(^{-1}\) for restoration of a diverse macrophyte community via transplantation for shallow, still waters. Novak and Chambers (2014) deduced that the efficacy of these thresholds is dependent on phosphorus limitation. Moreover, they suggested that multiple interventions, together with LMB treatment might be required to achieve the restoration goals.

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

Considering consumer community trends, any significant change either in structure, or in biomass, in fish or zooplankton communities was not detected in the above cited case of Loch Flemington (Meis, 2012), but the high uncertainty associated with monitoring fish makes detection of field scale responses difficult, especially over relatively short time scales. In Lake Rauwbraken (Netherlands), after a ‘Flock and Lock’ treatment using a combination of PAC and LMB the zooplankton *Daphnia galeata* temporary disappeared from the water column one week after the application, and reappeared after three months (Van Oosterhout and Lurling, 2011). Moreover, the loss of one generation of perch (*Perca fluviatilis*) was demonstrated. Nonetheless these effects were temporary. In this case, the disappearance of the cladoceran *Daphnia galeata* was related to a combination of physical effects of flocks, grazing inhibition of flocks and clay, abatement of food resources and absence of refuge from predation. An acute toxicity of LMB components or aluminum, used together with LMB under the “Flock and Lock” technique was excluded. A single study (Bishop et al., 2014) investigated the resident benthic community variation in terms of taxa richness, diversity, tolerance and functional feeding group composition upstream, in the inflow, and downstream, in the outflow, of Laguna Niguel lake, California. No substantial
variations were found before and for four days after the LMB application (approximately 112 mg L\(^{-1}\)).

### 4. Implications of LMB use for environmental and human health

#### 4.1 Evidence from ecotoxicological studies

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

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

Remarkably few studies have assessed the ecotoxicological effects of LMB on primary producers in the form of macrophytes or algae. At doses above 0.5 g L\(^{-1}\) LMB growth rates of both the green alga *Scenedesmus obliquus* and the cyanobacterium *Microcystis aeruginosa* were strongly
hampered (Van Oosterhout and Lürling, 2013). LMB leachates had little effect on growth of these organisms and also the effect of La concentrations comparable to La in the LMB doses had much less effect on phytoplankton growth. The authors ascribed the larger effect of LMB to the presence of the bentonite particles (Van Oosterhout and Lürling, 2013).

When assessing the toxicity of LMB, it has to be considered that the effect may be related not only to the potential release of La $^{3+}$ ions, but also to a physical effect of clay on the organisms living within the receiving waters. At the field scale, one target effect is the reduction of phytoplankton biomass as a result of flocculation, precipitation and P reduction (Lürling and Tolman, 2010; Van Oosterhout and Lürling, 2013). However, other non-target effects have been reported. Laboratory experiments have demonstrated a reduced grazing activity of *Daphnia galeata* (Van Oosterhout and Lürling, 2011); this may be caused by the initial high turbidity, which is known to reduce feeding rates in *Daphnia* (e.g. Kirk, 1991); or it could be associated with the reduced Chl-a values, i.e. lower food availability. The latter explanation is supported by the experiments by Lürling and Tolman (2010), who found that in the presence of phosphorous the formation of rhabdophane in a test solution of lanthanum nitrate caused a precipitation of algae (added as food), with a consequent reduction in *D. magna* growth. Population growth rate for the planktonic rotifer *Brachionus calyciflorus* was reduced at LMB concentrations of 200 mg L$^{-1}$ or higher (Van Oosterhout and Lürling, 2013). As LMB concentrations during and shortly after the surface addition from a barge will be much higher than the estimated EC$_{50}$ (half maximal effective concentration) for growth inhibition (154 mg L$^{-1}$), a field application of LMB may have a negative effect on rotifers. In general terms, Spears et al. (2013b) defined on the basis of the cited 16 case studies the range of observed values of suspended solids (0.62–46.0 mg L$^{-1}$) estimated during an LMB application, which overlaps the concentrations found to cause significant effects on a wide range of organisms (Bilotta and Brazier, 2008). These values, although temporary, may be not compatible with the water quality standards for short term exposure (24 h) defined by Canadian, EU or USA regulations, expressed as increased concentrations relative to background levels and ranging from 2
to 25 mg L\(^{-1}\). There is a need, therefore, for further assessment of the physical effects of LMB on aquatic organisms, considering also exposure duration and frequency, which strongly determine the overall effect of suspended solids. Even though suspended solid concentrations can reach pre-application conditions rapidly after an application; short-term durations of elevated concentrations following an application are theoretically sufficient to impair productivity in macrophytes and algae, or to cause mortality of young fish (Bilotta and Brazier, 2008). In general, major effects may be hypothesized for lithophilic fish species, especially if suspended solid deposition occurs during the reproductive phase, egg development or fry growth (November-January for salmonids, but also spring for lithophilic cyprinids). On the contrary, effects on cladoceran or copepod species were demonstrated for concentrations one order of magnitude higher than those usually occurring during LMB applications (Bilotta and Brazier, 2008). Concerning the effects of turbidity on benthic organisms, available information is usually biased towards lotic ecosystems, and the little information available for lakes is not sufficient to draw any conclusion. In Loch Flemington, a reduction of abundance of Chironomidae, Oligochaeta and Sphaeriidae, together with an increase of Trichoptera (Meis, 2012), were observed in the first year after LMB application. Nevertheless, the role of fine inorganic sediment deposition could not be disentangled from other possible effects, such as the reduction of trophic status, or direct La toxicity in this field study. Toxicity has been evaluated also in terms of responses to leachate La, after a LMB treatment. Concentrations of filterable La during and shortly after application may be much higher than the estimated thresholds (Van Oosterhout and Lürling, 2013). For example, according to Van Oosterhout and Lürling (2011), the maximum Filterable La (Fla) concentration measured in Lake Rauwbraken was 90.8 µg FLa L\(^{-1}\), which is close to the estimated chronic NOEC (No observed effect level) on reproduction for *Daphnia magna*, with potential effects on reproduction. As well, the average concentration of LMB in the lake was 67 mg L\(^{-1}\) during application, a value close to the concentrations affecting growth in juvenile *Daphnia* after 5 days exposure (> 100 mg L\(^{-1}\) according to Lürling and Tolman, 2010). Spears et al. (2013b) reviewed La concentrations during and after
LMB applications in 16 lakes. FLa values in surface water reached peaks up to 0.414 mg La L\(^{-1}\), exceeding for example the 48 h-EC\(_{50}\) for *Ceriodaphnia dubia* of 0.08 mg La L\(^{-1}\) but not the 48 h-EC\(_{50}\) of 5.00 mg La L\(^{-1}\) found by Stauber (2000) and Stauber and Binet (2000). FLa values were higher in surface waters than in bottom waters (peaks up to 0.100 mg La L\(^{-1}\), but at present information on toxicity of La for benthic organisms is scarce. Spears et al. (2013b) reported on the LMB, Total La (TLa) and FLa concentrations occurring in the surface and bottom waters of 16 treated lakes. Maximum surface water of TLa and FLa concentrations ranged between 0.026 mg L\(^{-1}\) and 2.30 mg L\(^{-1}\) and 0.002 mg L\(^{-1}\) to 0.14 mg L\(^{-1}\), respectively. Chemical equilibrium modelling indicated that the concentrations of La\(^{3+}\) ions never exceeded 0.0004 mg L\(^{-1}\) in lakes of moderately low to high alkalinity (>0.8 mEq L\(^{-1}\)), but that La\(^{3+}\) concentrations had the potential to reach 0.12 mg L\(^{-1}\) in lakes characterised by very low alkalinity.

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

Another concern is the potential release of other toxic substances from the LMB. For example, some authors found the release of trace metals (Lürling and Tolman, 2010) and NH\(_4^{+}\) (Reitzel et al. 2013b, Van Oosterhout and Lürling, 2013) in the LMB leachate, therefore, further investigation is needed in order to assess the release of impurities in natural waters. Nonetheless, according to the present knowledge, post application adverse effects caused by eventual impurities have not been reported.

Some experiments have focused on the potential bioaccumulation of La in aquatic organisms. Van Oosterhout et al. (2014) treated *Procambarus fallax f. virginalis* with an application of 1 g LMB L\(^{-1}\)
and measured the bioaccumulation of La in the crayfish after 14 and 28 days. They found a strong increase in concentrations in the ovaries, hepatopancreas and abdominal muscle, showing that La released from LMB is bioavailable for crustaceans. The uptake may occur through permeable body surface, gills and/or contaminated food. La bioavailability was found for the duckweed *Sperolleta polyrrhiza*, the frogbit *Hydrocharis dubia*, *D. magna*, the shellfish *Bellamya aeruginosa* and goldfish exposed to lanthanum nitrate, with bioconcentration factors up to 138 (Yang et al., 1999, Xu et al. 2012). Qiang and Xiao-rong (1994) measured La concentrations in *Cyprinus carpio* after 5-45 days exposure at 0.5 mg L\(^{-1}\) of lanthanum nitrate. They found bioconcentration factors up to 18 and 91, respectively, in gills and internal organs. Hao et al. (1996) evaluated the elimination period of La from different parts of the body. They found two different forms of La: one, accounting for 50-70% of total La, unbound to tissues, which can be eliminated in short periods (< 1 day) and another form tightly bound to tissues, which is eliminated after a longer time (half-lives up to 693 day in the skeleton). Landman et al. (2007) documented in a whole-lake LMB application a significant La accumulation in fish liver and hepatopancreas, but low concentrations in the flesh (cited in Hickey and Gibbs, 2009).
**Table 2 - Summary of the most informative ecotoxicological thresholds estimated for Lanthanum**

Modified Bentonite (LMB) and Lanthanum. EC$_{50}$=50% Effect Concentration (mg L$^{-1}$); NOEC=No Effect Concentration (mg L$^{-1}$); LOEC= Lowest Observed Effect Concentration (mg L$^{-1}$)

<table>
<thead>
<tr>
<th>Test organism</th>
<th>Test conditions</th>
<th>Stressor</th>
<th>Endpoint</th>
<th>EC$_{50}$ NOEC</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zooplankton</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Daphnia carinata</em></td>
<td>LaCl$_3$, solution, soft water, 48 hours</td>
<td>FLa</td>
<td>Mortality</td>
<td>0.04</td>
<td>Barry and Meehan, 2000</td>
</tr>
<tr>
<td><em>Daphnia carinata</em></td>
<td>LaCl$_3$, solution, hard water, 48 hours</td>
<td>FLa</td>
<td>Mortality</td>
<td>1.18</td>
<td>Barry and Meehan, 2000</td>
</tr>
<tr>
<td><em>Daphnia carinata</em></td>
<td>LaCl$_3$, solution, hard water, 6 days</td>
<td>FLa</td>
<td>Survival, growth</td>
<td>&lt;0.06</td>
<td>Barry and Meehan, 2000</td>
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<tr>
<td><em>Daphnia magna</em></td>
<td>not specified, solution, 48 hours</td>
<td>FLa</td>
<td>Reproduction</td>
<td>24</td>
<td>Sneller et al., 2000</td>
</tr>
<tr>
<td><em>Daphnia magna</em></td>
<td>La(NO)$_3$3•6H$_2$O, food suspension, P-containing medium, 14 days</td>
<td>FLa</td>
<td>Growth (length)</td>
<td>LOEC = 0.1</td>
<td>Lürling and Tolman, 2010</td>
</tr>
<tr>
<td><em>Daphnia magna</em></td>
<td>LaCl$_3$, solution, hard water, 21 days</td>
<td>FLa</td>
<td>Reproduction</td>
<td>0.1</td>
<td>Sneller et al., 2000</td>
</tr>
<tr>
<td><em>Daphnia magna</em></td>
<td>LMB, suspension, 5 days</td>
<td>LMB</td>
<td>Juvenile growth (weight)</td>
<td>871</td>
<td>Lürling and Tolman, 2010</td>
</tr>
<tr>
<td><em>Daphnia magna</em></td>
<td>LMB, suspension, 5 days</td>
<td>LMB</td>
<td>Juvenile growth (length)</td>
<td>1557</td>
<td>Lürling and Tolman, 2010</td>
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<tr>
<td><em>Daphnia magna</em></td>
<td>LMB, suspension, 48 hours</td>
<td>LMB</td>
<td>Immobilization</td>
<td>&gt;5000</td>
<td>Martin and Hickey, 2004</td>
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<td><em>Daphnia magna</em></td>
<td>LMB, suspension, 48 hours</td>
<td>LMB</td>
<td>Mortality</td>
<td>4900</td>
<td>Watson-Leung, 2008</td>
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<td><em>Ceriodaphnia dubia</em></td>
<td>LaCl$_3$, solution, 48 hours</td>
<td>FLa</td>
<td>Immobilization</td>
<td>5</td>
<td>Stauber and Binet, 2000</td>
</tr>
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<td><em>Ceriodaphnia dubia</em></td>
<td>LaCl$_3$, solution, 7 days</td>
<td>FLa</td>
<td>Reproduction</td>
<td>0.43</td>
<td>Stauber and Binet, 2000</td>
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<td><em>Ceriodaphnia dubia</em></td>
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<td>FLa</td>
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<td>0.08</td>
<td>Stauber, 2000</td>
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<td><em>Ceriodaphnia dubia</em></td>
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<td>Mortality</td>
<td>0.82</td>
<td>Stauber, 2000</td>
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<td>FLa</td>
<td>Reproduction</td>
<td>0.28</td>
<td>Stauber, 2000</td>
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<td><em>Ceriodaphnia dubia</em></td>
<td>LMB, Leachate, 48 hours</td>
<td>LMB</td>
<td>Immobilization</td>
<td>&gt;50</td>
<td>ECOTOX, 2008</td>
</tr>
<tr>
<td><em>Ceriodaphnia dubia</em></td>
<td>LMB, suspension, 7 days</td>
<td>LMB</td>
<td>Immobilization and reproduction</td>
<td>&gt;1</td>
<td>ECOTOX, 2008</td>
</tr>
<tr>
<td><em>Brachionus calyciflorus</em></td>
<td>LBM, suspension, 48 hours</td>
<td>LMB</td>
<td>Population growth rate</td>
<td>154</td>
<td>Van Oosterhout and Lürling, 2013</td>
</tr>
<tr>
<td>Fish</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td><em>Melanotaenia duboulayi</em></td>
<td>LaCl$_3$, solution, 96 hours</td>
<td>FLa</td>
<td>Immobilization</td>
<td>&lt;0.6</td>
<td>&lt;0.6</td>
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<td><em>Oncorhynchus mykiss</em></td>
<td>LMB, suspension, 48 hours</td>
<td>LMB</td>
<td>Mortality</td>
<td>&gt;13600</td>
<td>Watson-Leung, 2008</td>
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<tr>
<td>Macroinvertebrates</td>
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</tr>
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<td><em>Hyalella azteca</em></td>
<td>LaCl$_3$, solution, soft water, 7 days</td>
<td>FLa</td>
<td>Mortality</td>
<td>0.02</td>
<td>Borgmann et al., 2005</td>
</tr>
<tr>
<td><em>Hyalella azteca</em></td>
<td>LaCl$_3$, solution, hard water, 7 days</td>
<td>FLa</td>
<td>Mortality</td>
<td>1.67</td>
<td>Borgmann et al., 2005</td>
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<td><em>Hyalella azteca</em></td>
<td>LMB, suspension, 14 days</td>
<td>LMB</td>
<td>Survival and growth</td>
<td>&gt;3400</td>
<td>Watson-Leung, 2008</td>
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<tr>
<td><em>Hexagenia sp.</em></td>
<td>LMB, suspension, 21 days</td>
<td>LMB</td>
<td>Survival and growth</td>
<td>&gt;450</td>
<td>Watson-Leung, 2008</td>
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<td><em>Chironomus dilutus</em></td>
<td>LMB, suspension, 38 days</td>
<td>LMB</td>
<td>Survival and growth</td>
<td>&gt;450</td>
<td>Watson-Leung, 2008</td>
</tr>
<tr>
<td><em>Chironomus zealandicus</em></td>
<td>LMB, suspension, 38 days</td>
<td>LMB</td>
<td>Survival, emergence, sex ratio</td>
<td>&gt;400</td>
<td>400</td>
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<td>Nematodes</td>
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<td><em>Caenorhabditis elegans</em></td>
<td>LaCl$_3$, solution, 72 hours</td>
<td>FLa</td>
<td>Growth, reproduction</td>
<td>1.39</td>
<td>Zhang et al., 2010</td>
</tr>
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<td>Macrophytes</td>
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</tr>
<tr>
<td><em>Hydrocharis dubia</em></td>
<td>La(NO)$_3$3, solution, 7 days</td>
<td>FLa</td>
<td>Chlorophyll content</td>
<td>2.78</td>
<td>Xu et al., 2012</td>
</tr>
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<td><em>Hydrilla verticillata</em></td>
<td>La(NO)$_3$3, solution, 10 days</td>
<td>FLa</td>
<td>Chlorophyll content, oxidative stress</td>
<td>1.39</td>
<td>Wang et al., 2007</td>
</tr>
</tbody>
</table>
4.2 Human health implications of LMB use

Regulatory bodies in Australia such as the NICNAS (National Industrial Chemical Notification and Assessment Scheme) have considered LMB as a non-toxic product (NICNAS 2001). This initial toxicity assessment of LMB was based on dissolved/bioavailable lanthanum in the water body after a LMB application. Most of our knowledge on potential health effects of lanthanum carbonate arises from the studies related to the use of the phosphate binding agent Fosrenol® (lanthanum carbonate hydrate) used in patients with impaired renal function, in particular those undergoing dialysis (Komaba et al., 2015; Hutchison et al., 2009; Behets et al., 2004a). Lanthanum carbonate dissociates in the acid environment of the upper gastrointestinal tract to release lanthanum ions that allow the formation of the insoluble lanthanum phosphate which is eliminated in the feces.

The oral bioavailability of lanthanum is low (< 0.001%) (Damment and Pennick 2008). The small absorbed fraction is excreted predominantly in bile, with less than 2% being eliminated by the kidneys (Pennick et al., 2006). With almost complete plasma protein binding, La$^{+3}$ concentrations in patients receiving doses up to 3 g day over several years at steady state are <3 ng L$^{-1}$ (Damment and Pennick 2008). These properties greatly reduce systemic exposure, tissue deposition and the potential for adverse effects.

Due to its affinity for phosphate, lanthanum is considered a bone-seeking element. Using appropriate rat models of chronic kidney disease evidence was provided that lanthanum did not exert a direct detrimental effect on bone (Behets et al., 2004b, Bervoets et al., 2006) and La did not accumulate at critical sites of bone mineralization formation (Behets et al., 2005). On the contrary, La was found to reduce the biochemical and mineral abnormalities in bone related to chronic kidney disease (Damment et al., 2011). La carbonate-treated dialysis patients showed almost no evolution toward low bone turnover nor did they experience any significant accumulation of La in bone or blood or any aluminum-like effects on bone (D’Haese et al., 2003). Studies in rats and animals also reported therapeutic use of lanthanum carbonate to reduce aortic calcifications (Neven et al., 2009; Ohtake et al., 2013).
The liver is the main excretory organ of La. Within the liver, lanthanum has been observed in lysosomes particularly in close proximity to and, also, within the bile canaliculi but not in or attached to any other subcellular organelle (Bervoets et al., 2009). Lysosomes ultimately result in the cellular release of La into bile (exocytosis). Clinical studies with up to 6 years of follow-up have not disclosed any hepatotoxic effect of the drug in patients treated with this lanthanum carbonate (Hutchison et al., 2009).

Although from an ultrastructural point of view one would not readily expect La to be able to traverse the tight junctions in the blood-brain barrier, some concern has been raised about the elements potential accumulation in this organ, thereby linking potential brain toxicity of La to the neurological disorders reported with aluminum; i.e. dialysis dementia (Arieff 1985) and Alzheimer’s disease (Walton 2014). In studies to investigate possible neurotoxic effects of La exposure, La was determined in several regions of the brain after administration of intravenous 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 could be detected (less than 6 ng g$^{-1}$), this despite the fact that in the rats having received La intravenously, the median plasma La concentration was >300-fold higher than that seen in experiments after oral loading (Persy et al., 2006; Damment et al., 2009). Evaluation of cognitive function over a 2-year time period in patients on dialysis receiving lanthanum carbonate did not reveal any additive effect of La upon deterioration inherent to aging and dialysis treatment (Altmann et al., 2007). Nevertheless, based on data from experimental studies, Feng et al. (2006a and b) and He et al. (2008) warned against the potential of neurotoxicity associated with La exposure. Based on the results from these studies NICNAS assessed the risk related to the use of LMB in a Secondary Notification report (NICNAS 2014). However, results of these studies should be interpreted with caution, as no direct neurotoxicity end-point was evaluated and observed changes in the parameters under study were rather marginal and/or a clear dose-response relationship was lacking.
Exposure to La when used therapeutically is several orders of magnitude higher compared to the concentrations humans are potentially exposed to via intake of water treated with LMB (i.e. lanthanum carbonate daily dose 375-4500 mg). Indeed patients treated with lanthanum carbonate for phosphate control receive daily doses varying between 375-4500 mg whilst, according to Spears et al. (2013b), maximum FLa peak levels during and shortly after application of LMB lakes do not exceed 0.414 mg La L^{-1}. Hence, in a worst case scenario assuming a daily water intake of 1.5 liter day^{-1} exposure, this would correspond with a maximal intake of around 0.600 mg La day^{-1}; i.e. 625 times lower than the lowest dose used therapeutically. In an average application of LMB (such as 100 mg L^{-1}) the concentration of TLa would equate to 5 mg La L^{-1}. Assuming in a theoretical worst case scenario that 100% of La (5% La content in the LMB) will be leached out of the product and will not bind phosphate or other compounds, then a person would need to drink 300 L of the treated water per day to ingest the minimum dose of La that corresponds to the lowest lanthanum carbonate (Fosrenol®) daily intake. To reduce plasma phosphate levels to less than 6.0 mg dL^{-1} in uremic patients, normally the maximum daily dose of Fosrenol® required is 3000 mg and therefore the average person would need to drink 1200 L of treated water per day to ingest the maximum dose of La that is the Fosrenol® daily intake. Moreover, there is no reason to believe that La taken up via the drinking water would not bind phosphate in the gut and form an insoluble complex that will be eliminated via the feces. Hence, gastrointestinal absorption through exposure via drinking water as well as tissue accumulation will be extremely low posing no increased risk for possible health effects.

In a fish health monitoring report conducted in Lake Okareka (New Zealand) Landman et al. (2007) demonstrated that rainbow trout (Oncorhynchus mykiss) and koura (Paranephrops planifrons) accumulated La in the liver and hepatopancreas tissue, not in the flesh/muscle following the application of LMB. It was also demonstrated that La was removed from the fish liver and hepatopancreas tissues within a few months, suggesting a biological capacity of the fish to depurate La. This is in line with Bervoets et al. (2009) who demonstrated the hepatobiliary excretion of La in
rat studies. The highest total concentration of La measured in the liver and hepatopancreas tissue of trout in Lake Okareka after one and two months of LMB application was 1.2 and 0.8 mg kg\(^{-1}\) and the highest concentration of La in the hepatopancreas tissues of male and female trout was 0.8 and 1.0 mg kg\(^{-1}\), respectively (Landman et al., 2007). Therefore, in total the highest concentration of La in one trout was 2.0 mg kg\(^{-1}\). Thus, a person would need to consume 187.5 kg of fish per day to ingest the minimum daily dose of lanthanum carbonate (Fosrenol\®). Referring to the recommended maximum dosage of lanthanum carbonate an average person would need to consume 1500 kg of fish per day to consume the maximum dose of 3000 mg d\(^{-1}\). Considering that liver and hepatopancreas normally will not be eaten by humans, the risk to human health from consumption of fish harvested from a LMB treated water body is negligible.

5. Discussion

The results of the LMB application presented in this review underline a strong efficiency of this product in reducing the SRP concentrations in the water column and the P flux from sediments. This efficiency has been confirmed in laboratory, mesocosm and field trials. However, in the presence of high DOC concentrations SRP removal can be limited (Douglas, 2000; Lürling et al., 2014; Dithmer et al., this Issue) or even absent (Geurts et al., 2011). Also the interference with oxyanions other than PO\(_4\) was highlighted as a confounding factor (e.g. Reitzel et al., 2013a). However, in a recent study Dithmer et al. (this issue) did not find any correlation between alkalinity and P binding capacity of the LMB. Apart from these limitations the LMB efficiently binds SRP in fresh water ecosystems and over a wide range of physico-chemical conditions, with particular respect to pH. Maximum efficiency in P binding has been found in a 5-7 pH range, while the efficiency decreases markedly at pH higher than 9. Such high pH values are generally indicative of strong photosynthetic activity (potentially due to both macrophytes and phytoplankton) in eutrophic lakes. Under these conditions (and in particular during algal blooms) the sole LMB application is not recommended, because of the commonly observed high pH and low SRP concentrations,
making timing a crucial component of the application. Usually winter in temperate regions will offer the best window of opportunity with probably least side effects on biota. Also the use of this product in saline environments, cannot be a priori recommended due to potential lanthanum release as underlined by pre-commercialization studies (Douglas personal communication). In this way it has to be underlined that data on the LMB behavior in saline or brackish waters are scarce. In one of the few studies available, however, Reitzel et al. (2013a) found only a slight increase (< 1 %) of filtered TLa (La <0.2 µm), a 5 % increase of unfiltered TLa (La>0.2 µm) and 9 % of TLa adhering to the walls of the plastic tubes used in their tests in moderately saline water (15 ppt). These results indicate leakage of La from the clay matrix in moderate salinity water of about 15 %. At the moment the application of this product in even moderately saline environments need a careful risk and case by case evaluation. The results presented in this review allow to generalize this concept and to highlight the importance of carefully plan any field application and trial. In this way the results of the Deep Creek Reservoir are emblematic (NICNAS, 2014). A LMB trial was conducted in Deep Creek Reservoir, Australia in 2007 (Chapman et al., 2009, NICNAS, 2014). In this trial an approximately three times overdosing of LMB based on FRP concentrations occurred with a resultant maximum concentration of dissolved La of 220 µg L\(^{-1}\). Addition also occurred of other non-LMB agents that may have compromised the trial integrity. Temporally-associated fish mortalities occurred for up to two weeks post reagent application (NICNAS, 2014). Few living zooplankton individuals were identified in the reservoir seven weeks post-LMB application (NICNAS, 2014) with a possible link postulated between the LMB application and lethal effects on aquatic biota from two trophic levels.

Based on all available medical information, LMB can safely be applied in bathing water and drinking water reservoirs as long as these are not soft or acidic water bodies. From an ecotoxicological perspective, most studies indicate toxicity thresholds above the LMB and FLa concentrations reported after field scale applications (see sections 3.3 and 4.5 in this paper). Nonetheless, concentrations during and shortly after application may be closer or higher than the
estimated ecotoxicological thresholds, in particular for zooplankton species (*Brachionus calyciflorus, Daphnia magna* and *Ceriodaphnia dubia*), which proved to be the most sensitive among the organisms tested (Table 2).

Effects on benthic invertebrates, which are directly exposed to LMB through ingestion, need to be further explored. Potentially, the risk of La\(^{3+}\) persistence appears to increase under low alkalinity and low DOC concentrations and this should be considered further. Indeed, the presence of P or other ligands (e.g. HCO\(_3^{-}\), humic acids, OH\(^{-}\), etc.) in the water is an important factor when assessing the toxicity of lanthanum, altering the bioavailability of the metal. No obvious ecotoxicological effects were reported in field scale trials, although it should be noted that these effects are particularly difficult to quantify, comprehensively, at the whole lake scale. It should be considered that LMB is generally applied in lakes with high trophic state, where the presence of phosphorous or other ligands may reduce the bioavailability of FlA and other impurities, resulting in reduced toxicity potential.

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

Another concern is bioaccumulation of La in aquatic organisms, which was evaluated in crustaceans, macrophytes and fish. Bioconcentration factors up to 91 were found in the internal organs of fish (Qiang and Xiao-rong, 1994), but further experiments proved that most La accumulated can be eliminated in short periods (Hao et al., 1996; Landman et al., 2007). Longer
elimination times are needed for La accumulated in internal organs and skeletons. For this reason, potential toxicity at higher trophic levels (e.g. apex predators) should be evaluated.

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

In general, ecological recovery following eutrophication control has been well described in the literature (Brooks et al., 2001; Jeppesen et al., 2005; Rossaro et al., 2011; Verdonschot et al., 2013). A minimum of a few to some tens of years for recovery were indicated overall (Jeppesen et al., 2005; Verdonschot et al., 2013). Nevertheless, the number of studied cases showing recovery times of trophic status as fast as those typically observed in the case of LMB applications is minimal. Consequently, any robust comparison of biological responses is difficult, and forecasting the ecological responses after LMB applications remains challenging, as exemplified by the studies of Novak and Chambers (2014) and Gunn et al. (2014). Moreover, other confounding drivers, such as climatic perturbations (Moos et al., 2014) or the competition by exotic species (Gunn et al., 2014) may hamper the recovery of acceptable communities. The potential confounding effects of invasive species on ecological restoration is a remarkable question in freshwater ecology (van der Wal et al., 2013; Pires et al., 2007; Villeger et al., 2014).

Furthermore, the sudden trophic reduction (e.g. food availability) caused by geoengineering techniques may lead to the temporal disappearance of taxa, such as large bodied cladocera or
juvenille fish (Van Oosterhout and Lürling, 2011). However, as evidenced from the shock therapies in Lake Rauwbraken and Lake De Kuil, the resilience of ecosystems may often compensate for these perturbations. It is noteworthy that forecasting the lake responses after LMB applications is crucial, for instance, in a policy perspective, since achieving pre-defined “good ecological status” is warranted by the parallel restoration of ‘reference’ or ‘unimpacted’ communities for many groups, such as phytoplankton, fish or macrophytes (i.e. in the case of the EU Water Framework Directive). From a management point of view, the restoration of ecosystem services is crucial where the ecological status reflects the conditions to fulfil these services. An evaluation of risks derived by the application of LMB may benefit from preliminary biodiversity surveys aimed at evaluating the presence of key or conservation relevant species, as well as exotic species. Similarly, the use of predictive tools, such as ecological trophic models, or retrospective paleoecological approaches may help to evaluate the uncertainties associated with restoration goals. In conclusions, the possibility of a long recovery period (Hickey and Gibbs, 2009; Zamparas and Zacharias, 2014), as already demonstrated in many lakes after external P loadings control (Romo et al., 2005; Villena and Romo, 2003), should be taken into account in a risk assessment evaluation. Particularly, doing nothing and therewith taking prolonged toxic cyanobacteria blooms for granted should be assessed against the potential positive and negative impacts of any management measure, including the use of LMB. This review will hopefully provide the evidence necessary to support such assessments. In general terms, however, it can be argued that due to the multiplicity of environmental factors involved, the efficiency and the risk related to the application of the LMB are inevitably site-specific and the risks, in particular, can be minimized adopting specific measures accounting for the site specific variations (e.g. NICNAS, 2001). Cost may be a factor when considering using LMB in lake restoration. The price of lanthanum is of the order of thousands of dollars per ton, that is, for instance, around one order of magnitude higher than the cost of aluminum. The data presented in this paper, however, underline that LMB
phosphorus fixation (unlike the aluminum-mediated fixation) is highly stable under a wide range of physico-chemical conditions. Both techniques should be therefore considered as a tool available to the lake manager, whose use depends on site-specific circumstances definable only through a thorough system analysis.

6. Conclusions

- The majority of the data related to the efficiency of LMB indicated effective reduction of SRP concentrations in the water column and control of sediment SRP release, under most environmental conditions, and across laboratory, mesocosm and field scale trials in freshwater ecosystems.
- The operational performance of LMB is reduced in the presence of humic substances and in the presence of competing oxyanions in addition to PO$_4$$^{3-}$.
- The sole LMB application during strong photosynthetic activity (e.g. during algal blooms) is not recommended, due to the generally observed high pH and low SRP concentrations.
- The use of LMB in low alkalinity waters is not advised without thorough pretreatment testing to ensure that free La is not present in the water.
- The use of LMB in saline environments is not $a$ $priori$ recommended.
- La concentrations detected during or immediately after a LMB application are generally below acute toxicological threshold of different organisms, with the exception of zooplankton species (e.g. *Daphnia magna* and *Ceriodaphnia dubia*), however, short-term negative effects of suspended solids should be further examined.
- The human health risks associated with LMB treated surface waters appear to be negligible.
- There are no published examples of long-term negative ecotoxicological effects in LMB treated ecosystems. However, observed La uptake by organisms warrants longer-term investigation, especially at the field scale and particularly for sediment dwelling organisms.
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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