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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.

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, 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

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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 PO_4) 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 PO_4 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 La^{3+} to 1.00 Å for 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 $\mu g\ g^{-1}$) and Ce (80 $\mu g\ g^{-1}$) are similar to elements such as copper [Cu; 50 $\mu g\ g^{-1}$] and other elements like cobalt [Co; 23 $\mu g\ g^{-1}$], and lead [Pb; 20 $\mu g\ g^{-1}$] 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 [Yb; 2.8 $\mu g\ g^{-1}$]. 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., 1974). 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 coexisting 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 (1 m diameter) and large (6 m 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 $\mu g\ P\ L^{-1}$) in pore water sediment cores were reduced by more than 98% in a 7 day batch-test and by 87–98% in a 48 h batch test conducted on surface water samples (initial SRP concentration range 20–450 $\mu g\ P\ L^{-1}$). Batch tests on wastewaters with SRP initial concentrations of 1130 to 5320 $\mu g\ P\ L^{-1}$ demonstrated removal percentages of greater than 99%.

In parallel with the field trials, continuing laboratory evaluation