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Bio-accumulation of lanthanum from lanthanum modified bentonite treatments in lake restoration☆

G. Waajen [a,*], F. van Oosterhout [b], M. Lürling [b,c]

[a] Water Authority Brabantse Delta, P.O. Box 5520, 4801 DZ Breda, The Netherlands
[b] Aquatic Ecology & Water Quality Management Group, Department of Environmental Sciences, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands
[c] Department of Aquatic Ecology, Netherlands Institute of Ecology (NIOO-KNAW), P.O. Box 50, 6700 AB Wageningen, The Netherlands

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ABSTRACT

Lanthanum (La) modified bentonite (LMB) is one of the available mitigating agents used for the reduction of the phosphorus (P) recycling in eutrophic lakes. The potential toxicity of the La from LMB to aquatic organisms is a matter of concern. In this study the accumulation of La was investigated in the macrophyte *Elodea nuttallii*, in chironomid larvae and in several fish species during periods up to five years following in situ LMB applications. The application of LMB increased the La concentration of exposed plants and animals. During the first growing season following LMB applications, the La content of *E. nuttallii* increased 78 fold (3.98–310.68 μg La g^{-1} DW) to 127 fold (2.46–311.44 μg La g^{-1}). During the second growing season following application, the La content decreased but was still raised compared to plants that had not been exposed. The La content of chironomids was doubled in the two years following LMB application, although the increase was not significant. Raised La concentrations in fish liver, bone, muscle and skin were observed two and five years following to LMB application. Liver tissues showed the highest La increase, ranging from 6 fold (0.046–0.285 μg La g^{-1} DW) to ~20 fold (0.080–1.886 μg La g^{-1}, and 0.122–2.109 μg La g^{-1}) two years following application and from 6 fold (0.046–0.262 μg La g^{-1}) to 13 fold (0.013–0.167 μg La g^{-1}) after five years in pelagic and littoral fish. The La content of the liver from *Anguilla anguilla* (eel) had increased 94 fold (0.034–3.176 μg La g^{-1}) two years and 133 fold (0.034–4.538 μg La g^{-1}) five years following LMB application. No acute and chronic effects of La accumulation were observed and human health risks are considered negligible. We advocate the long-term study of effects of La accumulation following future LMB applications.

1. Introduction

Eutrophication of water bodies is considered a major water quality problem, often resulting in detrimental cyanobacterial blooms (Smith and Schindler, 2009; Watson et al., 1997). In urban regions, cyanobacterial blooms are widespread and the reduction of such blooms is of major concern to water managers (Waajen et al., 2014). A prerequisite for the long-term reduction of cyanobacterial blooms is the reduction of nutrient loadings (Cooke et al., 2005; Jeppesen et al., 2012). Next to the reduction of external nutrient loadings, the reduction of the biologically available internal pool of nutrients is crucial, as this pool may hamper lake recovery for long periods (Søndergaard et al., 1999). In managing eutrophication, the focus is on the control of phosphorus (P) which is considered the key nutrient (Schindler et al., 2008).

Lanthanum modified bentonite (LMB, commercially available as Phoslock®) has a high P-binding capacity. LMB, which was developed by the Australian CSIRO (Douglas, 2002), can be an attractive means targeting the reduction of the sediment P-release and the inactivation of the water column associated P pool by the formation of poorly soluble lanthanum-phosphate (Copetti et al., 2016; Lürling and Van Oosterhout, 2013). Next to the P-binding capacity of LMB, it is important to take the ecotoxicological safety of its active ingredient lanthanum (La) into consideration. Uptake of dissolved La by aquatic organisms has been shown (Qiang et al., 1994; Yang et al., 1999) and the potential toxicity of La to aquatic organisms has been raised as a matter of concern (Barry and

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* Corresponding author.
E-mail addresses: g.waajen@brabantsedelta.nl (G. Waajen), jean.vanoosterhout@wur.nl (F. van Oosterhout), miquel.lurling@wur.nl (M. Lürling).

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Meehan, 2000). To overcome the potential toxicity of La, LMB incorporates the La into a bentonite matrix (Haghseresht, 2006). Being locked in the bentonite matrix, the La can either react with phosphate ions in the water or stay in the matrix (Ross et al., 2008). The storage of La in the bentonite matrix and the extreme low solubility of produced La-phosphate indicate no bioavailability of La from LMB and little toxicological risk has been suggested (Haghseresht, 2006), making LMB ecotoxicologically compatible (Copetti et al., 2016). Nevertheless, La may leach from LMB following application (Lürling and Tolman, 2010; Spears et al., 2013) and increased insight in its potentially unintended treatment consequences is needed (Douglas et al., 2016). Uptake of La from LMB by animals has been shown in the laboratory (Van Oosterhout et al., 2014) and following field application (Landman and Ling, 2006), however information on this topic is scarce. Next to the uptake of dissolved La, the ingestion of LMB has been suggested as a route for La to enter biota (Van Oosterhout et al., 2014). Bioavailability of La from LMB is a prerequisite for possible toxic effects. Because long-term information on bio-accumulation of La following LMB applications is lacking, we studied the La content of aquatic organisms from different trophic levels. This study presents the results of analyses of the La content of chironomid larvae, a selection of fish and the macrophyte *Elodea nuttallii* before and after field applications of LMB at Lake De Kuil (Waajen et al., 2016b), pond Dongen and pond Eindhoven (Waajen et al., 2016a), during periods up to five years following the application. We hypothesized that the presence of LMB in the water body does not increase the La concentration (μg g^{-1} DW) of exposed aquatic organisms.

2. Material and methods

2.1. Study sites, treatments and chemicals

Lake De Kuil (N 51° 37′ 22"; E 4° 42' 23") has an area of 6.7 ha, an average water depth of 4 m and a maximum water depth of 9 m. Part of the lake is a bathing site, while the rest of the lake is used for angling. Regularly occurring cyanobacterial blooms resulted in swimming bans and warnings. On 18 May 2009, 4.38 tonnes of $FeCl_3$ solution (44.8 mL $FeCl_3$ m^{-2}; $\rho = 1.46$ kg L^{-1}, 40% $FeCl_3$) were applied to the lake as flocculant. From 19 until 21 May 2009, 13.65 tonnes LMB (Phoslock®, 5% La) were applied to the surface of the lake and 28.35 tonnes LMB were injected into the hypolimnion (on average 0.627 kg LMB m^{-2}). Characteristics of Lake De Kuil and of the treatment are provided in detail in Waajen et al. (2016b).

In the shallow ponds Dongen (N 51° 37′ 48''; E 4° 56′ 28″) and Eindhoven (N 51° 48' 97''; E 5° 47' 66''), compartments of 210–400 m^2 each were constructed. In the compartments, from August 2009 until September 2011 treatments were tested managing the frequently occurring cyanobacterial blooms in the ponds:

1. Dredging + biomanipulation (DB)
2. Dredging + polyaluminiumchloride (PAC) + biomanipulation (DPB)
3. LMB + biomanipulation (LB)
4. LMB + PAC + biomanipulation (LPB)
5. Biomanipulation (B).

LMB (Phoslock®, 5% La) was applied in two compartments at pond Dongen on 4 September 2009 (0.75 kg LMB m^{-2}) and in two compartments at pond Eindhoven on 2 and 3 September 2009 (1.13 kg LMB m^{-2}), while at each pond one of the LMB-treated compartments additionally received the flocculant PAC (Aqua-PAC39, $Al_n(OH)_mCl_{3n-m}$; $\rho = 1.37$ kg L^{-1}, 8.9% Al, 21.0% Cl), 16.7 mL PAC m^{-2} at pond Dongen and 16.3 mL PAC m^{-2} at pond Eindhoven. The other compartments did not receive LMB. The LMB and the flocculants $FeCl_3$ and PAC for the three sites were supplied and applied by Phoslock Europe GmbH (Ottersberg, Germany).

At the start of the experiment, macrophytes were lacking in the compartments. Biomanipulation included the introduction of *Elodea nuttallii* (Nuttall's waterweed, also known as western waterweed) and fish stock control. Each biomanipulated compartment received 1 kg of locally collected fresh *E. nuttallii* (on 28 April 2010 at Dongen and on 29 April 2010 at Eindhoven), from locations that had not been treated with LMB. Fish were removed from the compartments 1–5 at the start of the experimental period. These compartments were stocked with roach (*Rutilus rutilus*) and pike (*Esox lucius*) from locations that had not been treated with LMB, at pond Dongen in July and August 2010 and at pond Eindhoven on 28 September 2009. Characteristics of both ponds and of the treatments are provided in detail in Waajen et al. (2016a).

2.2. Sampling and analysis

2.2.1. Lake De Kuil: chironomids and fish

Chironomid larvae were collected before (18 March 2009) and after the LMB treatment (30 June 2011) at 10 sites spread over Lake De Kuil with an Ekman-Birge sampler (top ~5 cm of the sediment). The chironomids were sorted out by sieving the sediment samples under running tap water and the density (n m^{-2}) was determined. After collecting the chironomids, they were rinsed under running tap water to remove potentially attached LMB from the outside. The chironomids were stored at −18 °C and then subsequently freeze-dried (−60 °C), grinded and dried for 12–16 h at 40 °C. According to protocol C8-E6 (Wageningen University, Aquatic Ecology and Water Management Group; based on Van Griethuysen et al., 2004), approximately 20 mg of dried sample was digested using successively 200 μl Ultrex HNO_3 (65%) and 100 μl H_2O_2 (30–35%) at 94 °C. After complete evaporation, 2 mL of nano pure water was added and the samples were mixed (Vortex). Thereafter, 1 mL of each sample was diluted with 9 mL 0.1 M Ultrex HNO3. The destruates were analyzed for La (ICP-MS, Laboratory of the Department of Soil Siences, Wageningen University).

Fish from different species present in Lake De Kuil (eel, *Anguilla Anguilla*; perch, *Perca fluviatilis;* roach, *Rutilus rutilus;* bream, *Abramis brama;* pike, *Esox lucius*; tench, *Tinca tinca*) were caught before (9 April 2009) and after the LMB treatment (28 September 2011, 28 August and 5 September 2014) using electrofishing (5 kW) and trawl fishing, by professional fishing companies (Visserijbedrijf P. Kalkman, Moordrecht, The Netherlands in 2009 and 2014; ATKB, Stellendam, The Netherlands in 2011). 1–6 specimens per species were collected at each sampling event. Roach was only caught in 2011. Length and fresh weight of the fish were measured (Table 1). As LMB particles or La may potentially get attached to the outside of fish, external tissue (a piece of the skin) and internal tissues (the liver, 4 cm of the spinal bone, 4–5 cm of the muscle from the tail) were dissected separately. The tissue samples were stored at −18 °C and then digested and analyzed for the La content, using the method described for chironomids.

2.2.2. Ponds Dongen and Eindhoven: macrophytes and fish

On 28 April 2010, before the stocking of macrophytes at ponds Dongen and Eindhoven, three samples were randomly taken from the stocking material of *E. nuttalli*. After the stockings, three samples of *E. nuttallii* were randomly taken with a garden rake from each compartment with macrophytes, at pond Dongen on 25 May 2010, 30 June 2010 and 23 August 2011 and at pond Eindhoven on