Lanthanum in Water, Sediment, Macrophytes and chironomid larvae following application of Lanthanum modified bentonite to lake Rauwbraken (The Netherlands)

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HIGHLIGHTS

- Lanthanum Modified Bentonite can be applied to reduce sediment P-release.
- La in water, sediment, biota was determined for Lake Rauwbraken (The Netherlands).
- Water column total phosphorus was reduced for 11 years from 134 mg L\textsuperscript{-1} to 14 mg L\textsuperscript{-1}.
- Filterable La increased from 0.02 to 44 mg L\textsuperscript{-1}; ten years later it was 0.4 mg L\textsuperscript{-1}.
- 91\% of the La resides in the sediment, <1\% was found in macrophytes.

ABSTRACT

Lanthanum Modified Bentonite (LMB; Phoslock\textsuperscript{a}) is used to mitigate eutrophication by binding phosphate released from sediments. This study investigated the fate of lanthanum (La) from LMB in water, sediment, macrophytes, and chironomid larvae in Lake Rauwbraken (The Netherlands). Before the LMB application, water column filterable La (FLa) was 0.02 µg L\textsuperscript{-1}, total La (TLa) was 0.22 µg L\textsuperscript{-1}. In sediment the total La ranged 0.03–1.86 g m\textsuperscript{-2}. The day after the application the maximum FLa concentration in the water column was 44 mg L\textsuperscript{-1}, TLa was 528 mg L\textsuperscript{-1}, exceeding the Dutch Maximum Permissible Concentrations (MPC) of 10.1 mg L\textsuperscript{-1} by three to fourfold. TLa declined below the MPC after 15 days, FLa after 75 days. After ten years, FLa was 0.4 mg L\textsuperscript{-1} and TLa was 0.7 mg L\textsuperscript{-1}. Over the post-application years, FLa and TLa showed statistically significant downward trends. While the LMB settled homogeneously on sediment, after 3 years it redistributed to 0.2–5.4 g La m\textsuperscript{-2} within shallow zones, and 30.7 g m\textsuperscript{-2} to 40.0 g La m\textsuperscript{-2} in deeper zones. In the upper 20 cm of sediment, La concentrations were 7–6702 mg kg\textsuperscript{-1} dry weight (DW) compared to 0.5–7.0 mg kg\textsuperscript{-1} before application. Pre-application anaerobic sediment release of FLa was 0.006 mg m\textsuperscript{-2} day\textsuperscript{-1}. Three months after the application it was 1.02 mg m\textsuperscript{-2} day\textsuperscript{-1}. Three years later it was 0.063 mg m\textsuperscript{-2} day\textsuperscript{-1}. Before application La in plants was...
1. Introduction

Eutrophication of freshwater lakes is considered the most important water quality problem worldwide (Smith and Schindler, 2009). Associated cyanobacterial blooms, and the mitigation thereof, constitute an omnipresent challenge to water managers. Mitigation of eutrophication has focused on phosphorus (P) control (Carpenter, 2008; Schindler et al., 2008, 2016). A concomitant reduction of external- and internal P loads is considered essential to effectively mitigate cyanobacterial blooms (Cooke et al., 2005; Hilt et al., 2006). Internal P loading from lake sediments often hampers the lake recovery for years to decades following external nutrient load reduction (Gulati and Van Donk, 2002; Schindler and Hecky, 2000; Sondergaard et al., 2001). Significant P loads can be reduced by sediment capping techniques that provide a physico-chemical barrier between the sediment and the overlying water column. To this end, aluminium-, calcium-, and iron-salts have long been applied as the remediation technique of choice (e.g. Cooke et al., 1993, 2005). Over the past two decades, however, solid-phase P sorbents as a geo-engineering tool have gained considerable interest (Spears et al., 2013). The application of lanthanum (La) modified bentonite (LMB, Phoslock<sup>®</sup>) is one of these techniques (Douglas et al., 1999, 2016; Robb et al., 2003). Lanthanum modified bentonite has been applied to over 200 water bodies worldwide. A review of a range of field scale applications indicated efficacy in reducing both water column filterable reactive phosphorus (FRP) and internal P loading (Copetti et al., 2016). To date 79 published studies have examined the role of LMB (Search performed in Scopus using search term “Phoslock<sup>®</sup>”, 20-04-2019) in eutrophication management, of which only 8 specifically addressed the La present in LMB. Studies have included testing the effect of La on zooplankton (Lürling and Tolman, 2010), effect of humic substance in La complexation (Lürling et al., 2014), incorporation of La in animals both in a laboratory study (Oosterhout et al., 2014), and after field application (Waanen et al., 2017a), the vertical distribution of La over the sediment following application (Meis et al., 2012, 2013), La:P ratios in the sediment of a LMB-treated lake (Yasseri and Epe, 2016) and the confirmation of the presence of rhabdophane (LaPO<sub>4</sub>·H<sub>2</sub>O) formation (Slade and Gates, 1999) in sediments of 10 treated lakes (Dithmer et al., 2016b).

So, while a large number of whole lake applications with LMB have been reported in the literature, few studies have focussed on the role of La, and in particular in longitudinal studies relevant to the annual inputs and cycling of P in aquatic systems. Insight in the behaviour and fate of La is important to determine treatment efficacy, longevity, and the occurrence, if any, potentially undesirable side-effects.

In The Netherlands La is subjected to a maximum permissible concentrations (MPC) legislation (Sneller et al., 2000) that is applied to both the water column and sediments. In freshwater systems the Dutch MPCs are 10.1 μg L<sup>−1</sup> for nominally filterable (<0.45 μm) La, and 150.1 μg L<sup>−1</sup> for total La in the water column, while for sediment the MPC is 500.1 mg La kg<sup>−1</sup> DW (URL 1, Sneller et al., 2000). With these MPCs effectively regulating the application of LMB, there is a requirement for a detailed understanding of the distribution and concentrations of La in water, sediment and biota following LMB application. The rationale behind La determination, and the MPCs, is that ecotoxicology of La is assumed to occur in the dissolved form (e.g. La<sup>3+</sup>) in aqueous solution, where the trivalent La cation possesses the greatest risk for adverse biological effects (Das et al., 1988). In a recent study, however, Reitzel et al. (2017) demonstrated that “any La found in solution after LMB treatment in hard water lakes is associated with colloids.” In addition, it was demonstrated (Mucci et al., 2019) that in waters containing carbonate that La may be present as lanthanite ([La<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>·8H<sub>2</sub>O]) associated with the LMB, quite apart from that bound to phosphate as rhabdophane, or that bound by humic substances. On this basis, for many natural freshwaters, it would appear that little, if any La, is present in the uncomplexed, trivalent state. Nonetheless, further investigation of the nature (speciation) of La present in waters following LMB application, particularly over ecologically relevant timescales (years to decades) is required to further elucidate the potential for the biogeochemical transfer of La applied as LMB through water, sediment and biota.

In 2008, a combination of the LMB and the flocculent polyaluminium chloride (PAC) was tested in Lake Rauwbraken, the Netherlands to reduce internal P loading (Lürling and Oosterhout, 2013a). This study reports on the fate of La via the analysis of water column and sediment samples, in addition to that within macrophytes and chironomid larvae following the LMB application in Lake Rauwbraken. This study investigates the spatial and depth heterogeneity of the LMB, and the extent of Filterable La (FLa) release. A filtration experiment was used to test the hypothesis that part of FLa is particulate La.

2. Methods

2.1. Ethical statement

The treatment of Lake Rauwbraken with LMB (and low dose PAC as coagulant) was undertaken after permission was obtained from the owners of the lake (the Tilburg City Council), the water authority De Dommel and the bathing water authority of the Province Noord-Brabant.

2.2. Lake Rauwbraken

2.2.1. Application of the LMB

Lake Rauwbraken, located in southern Netherlands (Fig. 1A, B) has a surface area of 25692 m<sup>2</sup>, a mean depth of 8 m with a maximum depth 16 m, and an estimated volume of 208000 m<sup>3</sup>. A combined PAC and LMB treatment of Lake Rauwbraken was undertaken over 3 days, from April 21st to 23rd 2008. Two t of LMB were introduced as a P sorbent and ballast followed by two tons of PAC (buffered with 75 kg Ca(OH)<sub>2</sub>) to clear particulate matter from the water column. Thereafter, a further16 t of LMB were applied homogeneously to the lake surface from a GPS coordinated barge to act as an active P-sorbent barrier on the lakes bottom sediment. A more detailed description of this Flock & Lock application is given in Lürling and Oosterhout (2013a).

2.2.2. Water quality sampling

Water sampling was done using a submersible pump and hose (Reich, 12 V Tauchpumpe) in the south-western centre of the lake,
65 m from the shore (51°34’55.35” N, 5°07’52.14” E, Fig. 1C). From November 2005 to April 20th, 2008 samples were taken bi-weekly at 1 m depth intervals from the lake surface to bottom. In 2008 sampling was reduced to biweekly over depths 1, 3, 5, 7, and 10 m. From 2009 onwards, sampling was resumed at 1 m intervals. In 2009, sampling was done biweekly, while during 2010 the sample regime aimed at sampling once every 3 weeks, and in 2011 samples were taken every month. In 2012, the lake was sampled 5 times, in 2013 once, and from 2014 to 2017 3 times during summer.

On site, dissolved oxygen concentrations (mg L$^{-1}$) and saturation (%) were measured using a WTW- multi 350i meter (WTW GmbH & Co. KG, Weilheim, Germany). Water transparency was determined using a Secchi-disk. Two L water samples were brought to the laboratory, where turbidity was measured using a HACH 2100P turbidity meter (Hach Nederland, Tiel, The Netherlands). Chlorophyll-a (Chl-a) concentrations were measured by hot ethanol extraction spectrophotometric (NEN 6520) as described by Moed and Hallegraeff (1978) and/or with a PHYTO-PAM phytoplankton analyzer (HeinzWalz GmbH, Effeltrich, Germany) calibrated against the Dutch standard (NNI, 2011). Detection limit for the Dutch standard method is 5 µg L$^{-1}$ (NNI, 2011), for PHYTO-PAM it is 0.5 µg L$^{-1}$. A detailed description of the capacity of the PHYTO-PAM to distinguish between phytoplankton groups is given in (Lürling et al., 2018).

Total phosphorus (TP; µg L$^{-1}$) and total nitrogen (TN, mg L$^{-1}$) were measured in unfiltered water samples, filterable reactive phosphorus (FRP; µg L$^{-1}$), ammonium-N (AMM; mg L$^{-1}$) and nitrite + nitrate (NN) were determined in filtered water samples (0.45 µm membrane filters, Whatman NC45, Whatman International Ltd., Maidstone, UK) using a Skalar SAN + continuous flow analyzer (Skalar Analytical B.V., Breda, The Netherlands) following Dutch standard protocols (NNI, 1986, 1990, 1997). Nutrient concentrations below level of detection were replaced by their respective values: TP 10 µg P L$^{-1}$ for SAN++ and 6 µg P L$^{-1}$ for ICP-MS; FRP 4 µg P L$^{-1}$ for SAN++, 1 µg P L$^{-1}$ for ICP-MS; TN 0.2 mg N L$^{-1}$; AMM 0.02 mg N L$^{-1}$ and NN 0.01 mg N L$^{-1}$.

Per variable all data (different dates and depths) were pooled for the pre- and post-treatment period and subjected to Kruskal-Wallis One Way Analysis of Variance on Ranks to reveal changes. Samples were filtered through 0.45 µm membrane filters (Whatman NC45, Whatman International Ltd., Maidstone, UK), analyzed for their FLa concentration. Unfiltered samples were used to measure TLa. Both FLa and TLa were measured via ICP-MS in the Chemical-Biological Soil Laboratory of the Department of Soil Sciences (Wageningen University, The Netherlands). The detection limit for FLa was 0.02 µg L$^{-1}$, for TLa it was 0.2 µg L$^{-1}$, the relative precision for replicate sample analyses was FLa 3%, TLa 6%.

For FLa and TLa monthly-based boxplots are presented for the whole study period. Post application trends were tested by Spearman Rank Order Correlation in SigmaPlot v.12.5. During the post-application period, 3 extreme values in FLa concentrations and two TLa concentrations were observed that were included in our analysis. The effect of the extreme TLa and FLa concentrations on the Spearman Rank Order Correlation were also investigated.

2.2.3. LMB sedimentation

In April 2008, shortly before the PAC and LMB application in Lake Rauwbraken, 16 PVC 40 cm long pipe sediment traps with a surface area of 5.1 cm$^2$ were suspended 1 m above the lakebed of Lake Rauwbraken. One set of four single sediment traps (Fig. 1D, series A) were equally spaced along a transect running across the lake from Northeast to South-West, and were deployed from April
20 to May 14, 2008. Four sets of sediment traps (Fig. 1D, series B) were equally spaced over the lake bottom from March 19 to May 21, 2008. The series B were four traps put on a small rig with the traps in close proximity. The entrances of traps A1 and A2 were at 12 m depth, A3 at 11 m and A4 at 7 m depth. Material collected in the sediment traps comprised flocculated suspended particulate material and sedimented LMB. Sediment trap samples were centrifuged (5000 rpm) and freeze-dried at -60 °C. From the dry material approximately 20 mg was digested in a combination of Ultrax HNO3 (65%) and H2O2 (35%) (Griethuysen and Moermond, 2000). La concentration in the sediment trap digestes was determined by ICP-MS at the Chemical-Biological Soil Laboratory of the Department of Soil Sciences (Wageningen University Research Centre).

Lanthanum concentrations measured in the digested sediment trap material was used as a tracer to determine the spatial distribution of the LMB after the application. Based on the total of 18 t of applied LMB to the 25692 m² of lake surface, it is expected that ca 0.7 kg LMB m⁻² will settle homogeneously on the lake bottom (Assuming a 5% La (w/w) concentration in the LMB, this gives an estimated concentration of 35 g La m⁻²). The distribution of LMB using La as a tracer was evaluated using a Kruskal-Wallis one-way ANOVA on ranks in SigmaPlot v.12.5, with the location of the sediment traps as factor.

2.2.4. Spatial distribution of sedimentary lanthanum

Two intact sediment cores were sampled prior to the LMB and PAC application (April 13, 2008). Three years after the application (2011), 46 intact cores were sampled along a transect (Fig. 1E) using an UWITEC (Umwelt und Wissentechnik Richard Niederreiter, Weissensteinstrasse 30, 5310 Mondsee, Austria) core sampler. In 2011, replicate cores were sampled at 1 m water depth intervals and fixed distances from shore from just above the water's edge down to 14 m water depth (90 m offshore). While depths 5 and 10 m were not obtained, the sampling yielded two cores for 9 m depth; 3 cores for 0, 1, 3, 4, 11, 12 and 13 m depth; 4 cores for 7 and 8 m depth, and 6 cores for 2 and 14 m depth. In all cores the thickness of the sediment layer was recorded. All sediment cores were divided in 2 cm subsamples. If <2 cm of sediment was present, the available amount was sampled. Sediment was defined as any material on top of the underlying sand. From the subsamples of the 2008 cores, approximately 1 g of wet sediment was subjected to a P-fractionation analysis according to Psenner et al. (1984), the La concentrations were determined in the extracts. The 2011 subsamples were subjected to the extraction method of Houba et al. (1997). Whereas the Psenner extraction uses a series of increasingly aggressive steps, the Houba method consists of one step of 15 mL of 0.43 M nitric acid added to approximately 1.5 g of dry sediment (dried at 30 °C), agitated for 2 h, centrifuged for 10 min at 3000 rpm, and filtered through a Whatman Aqua 30/0.45 CA filter Unit.

La concentrations in the extracts were determined by ICP-MS at the Chemical Biological Soil Laboratory of the Department of Soil Sciences (Wageningen University). For the Psenner (1984) La extractions, the ICP-MS detection limits (LOD) ranged from 0.002 to 0.3 µg L⁻¹ depending on the step. The La concentrations in the Houba et al. (1997) extraction were determined by ICP-AES with a LOD of 0.01 mg L⁻¹.

Wet (Mw, (g)) and dry sediment weights (Md, (g)) were determined after 24 h drying at 105 °C, from which the fraction of dry sediment (Fdry = Md/Mw, dimensionless) in the subsamples was calculated. For each subsample, the La concentration was calculated in mg kg⁻¹ DW. For the 2008 cores, this involved the summation of the five fractions (H2O, bicarbonate/dithionite, NaOH, HCl and final digestion with H2SO4). For each subsample, the amount of La present (Laub, (g)) was calculated based on the volume of the sediment subsamples, the surface area of the cores and the specific gravity (SG) of the sediment. The SG was estimated using SG = 1 + 1.2 Fdry (kg m⁻³), in which Fdry (dimensionless) is the fraction of dry material in the sediment subsample by regressing Fdry on the SG. The concentration of La (g m⁻²) in the sediment both pre- and post-LMB application, was estimated by summation of the (Laub, (g)) per core and scaled to (g m⁻²). The spatial distribution of La (g La m⁻² per depth) over the lake's bottom and within the sediment as mg La kg⁻¹ sediment per cm depth in the sediment are investigated.

2.2.5. Sediment lanthanum release

Undisturbed sediment cores were sampled at depths greater than 10 m using a UWITEC core sampler (50 cm long, 5 cm internal diameter) one week before LMB application (April 13, 2008; n = 5), two months after application (June 19, 2008; n = 5) and after 3.5 years (October 16, 2011; n = 6) (Fig. 1E). For the experiment in 2008, the cores (with their original overlying water) were stored for approximately two years in 4 °C in the dark to test both effectiveness and durability of the PAC-LMB treatment. This procedure was followed to test the durability without possible disturbance – e.g. wind or fish induced resuspension, or new sediment being formed on top of the treated sediment, which naturally occurs in lakes. The 2008 cores were all incubated under anaerobic conditions to test the worst-case scenario of enhanced P release under anoxic conditions. After a 2 y incubation, the overlying water was removed by syphon and replaced with Millipore 18 m² water after recording the overlying water volumes for each core. This procedure was repeated each day during 4 incubations of 24 h at 7 °C in the dark. Cores collected in 2011 were immediately subjected to the experimental conditions. In this case, 3 cores were incubated under anaerobic conditions and 3 under aerobic conditions. Oxygen free Millipore water was prepared by bubbling with nitrogen gas until the oxygen concentrations was below 0.04 mg L⁻¹, pH remained between 6.7 and 7.2. Oxygenated Millipore 18 m² water was prepared by aeration until 100% oxygen saturation was achieved. Samples of the prepared Millipore 18 m² water were used as control (2008 cores n = 4, 2011 cores n = 12) and processed as described for the lake water samples. For each core and incubation period, the total amount of FLa released (Ri) was computed by: Rij (µg) = [Xij] x Vi, with [Xij] the FLa concentration (µg L⁻¹) in core i during incubation period j, Vi the volume of water in the core i. With Ri (µg) = Sić(Ri), the total amount of FLa released during the experiment in core i, for each core i, the 24 h sediment release rates were computed as: R24i (mg m⁻² day⁻¹) = Sić(Ri) / 24, with A = surface area of the sediment in the core (0.00181 m²) and t = total duration (min) of the experiment.

The FLa release rates passed on normality (Shapiro-Wilk test) and equal variances (Levene’s test). T-tests were done in SigmaPlot v.12.5 to investigate any differences in FLa release before and after the LMB and PAC application (cores 2008) and between aerobic and anaerobic conditions (cores 2011).

2.2.6. Macrophytes

Leaves and roots of Nymphaea (floated leaf), Phragmites, Scirpus and Typha (emergent) were collected on April 20, 2008 (pre-PAC-LMB application), and August 5, 2008 (post application). The plant material was thoroughly rinsed with demineralized water. From the roots only, the inner tissue was selected to avoid possible attached LMB. All material was frozen immediately following collection and subsequently freeze dried. On October 12, 2008 and March 23, 2009 submerged macrophytes were sampled by scuba diving along a transect (Fig. 1F) from 1 to 9 m depth, (9 depths 12.10.2008) and 6 depths (23.03.2009). All macrophytes present
(Elodea nuttallii) were collected within a 0.5 m diameter area. The macrophytes were thoroughly rinsed with lake water at the time of sampling. After weighing, the material was dried in an oven at 50 °C. The macrophyte materials were digested and analyzed for their La concentration as described for the sediment traps.

2.2.7. Chironomid larvae

Chironomid larvae in the sediment were regularly sampled at 10 locations using an Ekman-Birge grabber (0.04 m²) along a transect across Lake Rauwbraken (Fig. 1G) from April 18, 2008 (shortly before the PAC-LMB application, one sample date) until May 15, 2011 (3 years after the application) with a total of 26 samplings. Upon return to the laboratory, the sediment samples were washed through a 0.5 mm sieve using tap water. The collected larvae were then thoroughly rinsed with Millipore water and visible particles on the outside of the larvae were removed. No attempt was made to clean the guts of the larvae. For each sample location the larvae were counted, pooled and freeze dried at ~60 °C. The digestion and analysis of the La in the chironomid larvae was undertaken as described for the sediment traps.

3. Results

3.1. Water quality variables

The LMB application in Lake Rauwbraken strongly reduced the water column chlorophyll-a concentration, the share of cyanobacteria, total phosphorus and nitrogen concentrations, filterable phosphorus concentration, and turbidity, while it increased Secchi depth and hypolimnic oxygen concentration / saturation (Table 1).

3.2. Water column La

In 2006/7, prior to the LMB application, the mean water column FLa concentration was 0.02 μg L⁻¹ (SD = 0.01 μg L⁻¹, n = 323), while the TLa was 0.22 μg L⁻¹ (SD = 0.32 μg L⁻¹, n = 323). One day after the application, the mean water column FLa was 44 μg L⁻¹ (SD = 35 μg L⁻¹; n = 5), while the TLa was 528 μg L⁻¹ (SD = 508 μg L⁻¹; n = 5), 2200 times and 2400 times the preceding FLa and TLa concentrations, respectively. Using a 3 parameter (FLa maximizing, FLa0, b) exponential decay model the decay rates were 0.04 day⁻¹ and 0.13 day⁻¹ for FLa and TLa, respectively (Appendix A).

During the post-application period (2009 and later), 3 extreme FLa concentrations (out of 622) and two extreme TLa concentrations, respectively. Using a 3 parameter (FLaF, FLa0, b) exponential decay model the decay rates were 0.04 day⁻¹ and 0.13 day⁻¹ for FLa and TLa, respectively.

During the post-application period (2009 and later), 3 extreme FLa concentrations (out of 622) and two extreme TLa concentrations (out of 603) were observed. The observed extreme values were: April 2, 2012 with 182 μg L⁻¹ of FLa at 3 m depth and 200 μg L⁻¹ of TLa at 9 m depth. On May 25, 2012 the FLa concentration at 3 m depth was 22 μg L⁻¹ and the TLa concentration at 10 m was 46 μg L⁻¹. On August 26, 2014, the FLa concentration at 2 m depth was 12.6 μg L⁻¹. Including the 3 extreme values the post-application FLa concentrations ranged from 0.05 μg L⁻¹ to 182 μg L⁻¹ with a mean of 2.0 μg L⁻¹ (SD = 7.6 μg L⁻¹, n = 622). Excluding the extremes, the FLa concentrations ranged from 0.05 μg L⁻¹ to 11.8 μg L⁻¹ with a mean of 1.7 μg L⁻¹ (SD = 2.02 μg L⁻¹, n = 619). Including the two extreme concentrations, the post-application TLa ranged from 0.20 μg L⁻¹ to 200 μg L⁻¹ with a mean of 5.5 μg L⁻¹ (SD = 9.8 μg L⁻¹, n = 603), excluding the extremes, FLa concentrations ranged from 0.20 μg L⁻¹ to 39.1 μg L⁻¹ with a mean of 5.1 μg L⁻¹ (SD = 5.5 μg L⁻¹, n = 601). While the overall post-application pattern is of a gradual decline in concentration, there are fluctuations in the monthly means of both FLa and TLa during the post-application period (Fig. 2). Initially, the FLa and TLa concentrations increase as a result of the LMB application. Taken over the whole post-application period (2008 and later) both TLa and FLa show a significant downward trend. For FLa and TLa the Spearman Rank Order Correlation with year were −0.77 and p < 0.01 (n = 10) and −0.73 and p < 0.01 (n = 10), respectively. Excluding the extreme values in FLa and TLa concentrations, the Spearman Rank Order Correlation were −0.78 for FLa and −0.77 for TLa, respectively (both p < 0.01).

3.3. LMB sedimentation

On May 14, 2008, 10.5 g La m⁻² (SD = 2.5 g m⁻², n = 4) and on May 21, 2008 16.2 g La m⁻² (SD = 2.8 g m⁻², n = 12) had settled (Fig. 1B). The Kruskal-Wallis one way ANOVAs on ranking (Hₐ) the differences between locations was not significant, i.e. on May 14 Hₐ = 3.0, p = 1.0 and on May 21 Hₐ = 7.7, p = 0.05. While the difference between May 14 and May 21 suggests not all LMB had settled on the bottom by May 14, the theoretical coverage of 35 g La m⁻² was not attained.

3.4. Spatial LMB distribution in lake bottom sediment

Along the transect (Fig. 1E), between 0 and 5 m depth–1 cm sediment (defined as any material on top of the underlying sand) was found. From 5 to 10 m the sediment layer was 2–5 cm thick and below 12 m the sediment was more than 15 cm thick (Fig. 3, top).

Before application, the La concentration between 0 and 5 m depth ranged from 0.03 g m⁻² to 0.07 g m⁻², between 5 and 10 m from 0.14 g m⁻² to 0.20 g m⁻² and below 10 m it ranged

| Variables | 2006–2007 | 2008 | 2009–2018 | Hₐ=2 | p |
|-----------|-----------|------|-----------|------|---|
| Chlorophyll-a (μg P⁻¹) | 16.5⁰ (32.4) | 706 | 4.92⁰ (12.13) | 330 | 5.66⁰ | 7.13 | 1188 | 350 | <0.01 |
| Cyanobacteria (%) | 64⁰ (32) | 411 | 19⁰ (17) | 263 | 17⁰ (22) | 1108 | 546 | <0.01 |
| Secchi depth (m) | 3.5⁰ (1.6) | 89 | 5.8⁰ (2.5) | 24 | 3.7⁰ (1.6) | 123 | 12 | <0.01 |
| Turbidity (NTU) | 5.4⁰ (7.5) | 557 | 2.1⁰ (1.9) | 264 | 2.2⁰ (1.7) | 1015 | 179 | <0.01 |
| TP (μg L⁻¹) | 134⁰ (132) | 363 | 13⁰ (11) | 123 | 14⁰ (14) | 1076 | 502 | <0.01 |
| TN (mg L⁻¹) | 0.96⁰ (0.99) | 303 | 0.6⁰ (0.71) | 101 | 0.48⁰ (0.37) | 933 | 70 | <0.01 |
| FRP (μg L⁻¹) | 20⁰ (50) | 436 | 5⁰ (6) | 125 | 6⁰ (11) | 1073 | 167 | <0.01 |
| AMM (mg L⁻¹) | 0.2⁰ (0.37) | 452 | 0.11⁰ (0.14) | 113 | 0.1⁰ (0.14) | 1036 | 14 | <0.01 |
| NN (mg L⁻¹) | 0.08⁰ (0.12) | 450 | 0.15⁰ (0.11) | 113 | 0.0⁰ (0.07) | 1036 | 61 | <0.01 |
| Hypo oxygen (mg L⁻¹) | 0.86⁰ (1.72) | 143 | 8.2⁰ (1.72) | 40 | 3.7⁰ (4.06) | 188 | 102 | <0.01 |
| Hypo oxygen sat (%) | 5⁰ (15) | 119 | 7⁰ (33) | 40 | 3⁰ (37) | 180 | 109 | <0.01 |
from 0.20 g m$^{-2}$ to 1.86 g m$^{-2}$ (Fig. 3, bottom). Three years after the application (2011), the sediment La concentration between 0 and 5 m depth ranged from 0.2 g m$^{-2}$ to 5.4 g m$^{-2}$, between 5 and 10 m from 24.7 g m$^{-2}$ to 30.6 g m$^{-2}$ and below 12 m from 30.7 g m$^{-2}$ to 40.0 g m$^{-2}$ (Fig. 3, bottom). At 11 m depth the sediment La concentration was lower relative to surrounding depths. These changes corresponded to mean increases in La concentrations in the 0 to 5 m, 5 to 10 m and below 10 m depth intervals of 56, 90 and 33 times respectively.

3.5. Vertical distribution of La in lake bottom sediment.

The pre-application La concentration slightly increased from 0.5 mg kg$^{-1}$ between 0 and 2 cm to 7 mg kg$^{-1}$ between 14 and 16 cm depth in the sediment (Fig. 4). The post-application La sediment concentrations decreased monotonically from 6702 mg kg$^{-1}$ between 0 and 2 cm to 7 mg kg$^{-1}$ between 12 and 14 cm. At 16 cm depth it was similar to background concentrations (Fig. 4). Based on an assumed La concentration of 5% La in the LMB this equates to the 0 to 2 cm layer post application containing approximately 13% LMB. This also corresponds to a 13,400 times increase in sediment La over pre-application concentrations.

3.6. Sediment release of Lanthanum

The average FLa release from the cores sampled before the application of LMB was 0.006 mg La m$^{-2}$ day$^{-1}$ (Table C.1, experiment 2008) that exceeds the LOD 0.003 mg m$^{-2}$ day$^{-1}$ based on the LOD for FLa. The post-application 2008 anaerobic release of FLa was 1.02 mg m$^{-2}$ day$^{-1}$ that was 17 times higher than the pre-application FLa release, $T_{df} = -3.39, p < 0.01$ (Table C.1, experiment 2008). In the core samples from 2011, the anaerobic release of FLa of 0.063 mg m$^{-2}$ day$^{-1}$ was lower than that measured in the 2008 post-application cores (Table C.1, experiment 2008). The FLa release under anaerobic conditions (0.063 mg m$^{-2}$ day$^{-1}$) was an order of magnitude higher than under aerobic conditions (0.006 mg m$^{-2}$ day$^{-1}$), $T_{df} = 8 = -3.39, p < 0.01$ (Table C.1, experiment 2011).

3.7. Macrophytes

In 4 species of emergent macrophytes (Nymphaea alba, Phragmites australis, Scirpus lacustris, Typha latifolia) collected before the application of the LMB in 2008 the La concentrations were between 0.82 and 5.05 mg La kg$^{-1}$ DW (Table D.1A). Post-application La concentrations were substantially elevated. For floating leaves and emergent macrophytes the increase was 6 to 130 times higher, ranging between 22.6 and 136 mg La kg$^{-1}$ DW, respectively. Before the LMB application the La concentration in the submerged macrophyte, Elodea nuttallii was 7.5 mg La kg$^{-1}$ DW. After the application DW concentrations increased up to 1764 and 2925 mg La kg$^{-1}$, corresponding to a 235 to 389 times higher La concentration, respectively (Table D.1B).

3.8. Chironomid larvae

Following the application of the LMB in 2008, the density of chironomus larvae fluctuated seasonally with higher numbers in winter, and lower numbers in summer (Fig. 5A). The La concentration in the chironomid larvae increased from 1.7 (SD = 0.6) μg g$^{-1}$ DW pre-application to 1421 (SD = 956) μg g$^{-1}$ DW one month after the application or 836 times the pre-application concentration (Fig. 5B). In the last sample (May 2011), La concentrations had decreased to 206 (SD = 81) μg g$^{-1}$ DW (Fig. 5B).
3.9. Lanthanum in the lake

In this study, 18 t LMB (4.5% La) were applied to Lake Rauwbraken in April 2008, equivalent to 810 kg La. We assume that during the application the LMB spread equally over the lake and shallow pool (810 kg on 30092 m²). This means about 132 kg La should have settled in the shallow pool, which leaves 678 kg for the lake. This is quite close to the 619 kg estimated in the sediment (Table E.1). The submerged macrophytes contained 2.4 kg La (2008) and 2.1 kg La (2009) and the water column TLa was 1.9 kg in 2009 with a loss to the groundwater of 0.2 kg.

4. Discussion

Long-term results following the application of LMB demonstrate not only effective reduction in FRP and TP, and hence trophic status, but also major improvements in water quality variables related to algal biomass and species composition, turbidity and nitrogen and oxygen concentrations. Based on OECD criteria, Lake Rauwbraken can be considered to have shifted from a eutrophic to a predominantly mesotrophic status. Detailed elaboration of water quality improvement and trends over the post treatment period will be presented elsewhere (Oosterhout et al., 2019).

Despite the demonstrable, and sustained improvement in water quality in Lake Rauwbraken following the application of LMB, the presence of and the fate of both TLa and FLa is worthy of a detailed investigation to satisfy concerns in terms of environmental fate and public acceptance of LMB as a viable in-lake eutrophication management option. This is also pertinent in light of the potential for trophic transfer of La (Oosterhout et al., 2014) and the potential, albeit slight, for La ingestion by recreational lake users (D’Haese et al., 2019).

Importantly, our results show that La was present in Lake Rauwbraken before the application of the LMB in 2008, in all water and sediment samples, macrophytes and chironomid larvae. This observation is consistent with Waajen et al. (2016b) and important
in view of the belief in the Netherlands that LMB application implies "the introduction of foreign substances to the water" (Deelen, 2013; Heerdt et al., 2012) that are "naturally absent in sediment" (Gogh, 2014). While lanthanum is a rare earth elements, its phosphate binding capacity is not affected by anaerobic conditions (Douglas et al., 2004; Ross et al., 2008). Significantly, however, anaerobic incubations revealed ten times more La release from LMB amended sediment than from aerobic incubated sediment cores. While the cause is not certain, it may be that Fe^{2+} ions formed under anaerobic conditions displace La from the interlayer. Recently, a relatively strong adsorption of Fe^{2+} by LMB has been found with maximum adsorption capacity of 8.5 mg Fe^{2+} g^{-1} LMB (Ding et al., 2018), similar to the La contained within LMB. Anaerobic conditions also stimulate methanogenesis and methane ebullition (Bergen et al., 2019), which could transport colloidal La from the sediment into the over-standing water. Evidently, more research is needed to decipher what is causing the elevated La release from amended sediments under anoxia.

The decline of FLa and TLa below their MPCs is important, because The Netherlands is the only country that has La standards for water and sediment (Sneller et al., 2000). The La MPCs were introduced because of industrial emission of rare earth elements in de Nieuwe Waterweg, the Netherlands (Sneller et al., 2000). The La standard is based on the No Observed Effect Concentration (NOEC) determined in a 21 days Daphnia reproduction test (NOTOX, 1995) divided by 10 (Sneller et al., 2000). The NOEC of 100 µg L^{-1} was calculated as the geometric mean (A × B)^{1/2}, with A and B as the limits of the exposure range (NOTOX, 1995), whereas using all six measurements presented in the NOTOX report yielded a mean of 232 µg L^{-1} and a median of 195 µg L^{-1}, thus, twice the NOEC used. More concerning is that in the experiment the animals were supposed to be fed daily with 1 × 10^6 cells mL^{-1} Chlorella, but from day 5 to 13 this was reduced to 0.5 × 10^6 cells mL^{-1}, where after the feeding with 1 × 10^6 cells mL^{-1} was restored (NOTOX, 1995). The animals were cultured in Elendt M7 medium that contains 0.143 mg L^{-1} K_2HPO_4 and 64.8 mg L^{-1} NaHCO_3 (Samel et al., 1999). Consequently, precipitation of algal food in the higher La treatments cannot be excluded (Lürling and Tolman, 2010). This seems to be corroborated by a Parallel Lines Analysis showing that the slopes of the cumulative reproduction in each NOTOX treatment was similar (F_{A,B} = 0.4769; P = 0.7524; Fig. 6). Evidently, the difference is caused in the first reproductive days until day 13 (Fig. 6). Hence, the Dutch La standards are based on a single experiment that suffers from a severe methodological flaw.

4.1. Sediment traps

The amounts of La retrieved in the sediment traps that were deployed during the treatment was substantially below the expected 35 g La m^{-2} – which equates to 700 g LMB m^{-2}. Based on the amounts of TLa in the water column it was expected that by May 14 and 21 a minimum of 34 g LMB m^{-2} had settled. The same sediment traps were used in 2007 and 2008 before the LMB application which yielded an average sedimentation rate of suspended solids of 25 g m^{-2} (SD = 15 g m^{-2}, n = 12) per 4 weeks. To sample these low rates of sedimentation, sediment traps with a small opening and a long tube are considered the best option (Bloesch and Burns, 1980). The entry of material into a sediment trap is hampered by friction, i.e. for each particle that settles in the trap an equal volume of water has to leave the trap. The latter is slowed down by friction of the water with the inner wall of the trap (Bloesch and Burns, 1980). Under low sedimentation rates this friction is not considered a major problem. However, after the LMB application in Lake Rauwbraken the majority of the approximately 700 g m^{-2} of the LMB settled within a few days. During such a massive sedimentation, the friction at the entrance of the traps is likely to cause parts of the material to be directed away from the trap (Bloesch and Burns, 1980). Thus, the traps may have underestimated the amounts of LMB (La) that settled on the sediment.

![Fig. 4. Sediment La profiles (log scale). whiskers indicate 1 SD, dashed vertical line indicates the sand bed below the sediment; 2008 = pre-application, 2011 = post-application.](Image)
4.2. Sediment-La

The spatial La distribution in the sediment revealed that, after the application, the first 6 cm of the sediment exceeded the MPC of 500.1 mg kg$^{-1}$ (Fig. 3). According to its manufacturers, the LMB should be homogeneously distributed over a lake’s sediment, moreover its placement on the sediment is described as a thin layer on top of the sediment – which then should result in its maximum effective sediment capping function. Yasseri and Epe (2016) reported that wind drift and internal currents may affect the spatial distribution of the LMB. While our results from the sediment traps indicated a homogeneous distribution of La over the lake’s sediment directly after the application, 3 years later La was redistributed from shallower to deeper parts of the lake with La contents of < 5.4 g m$^{-2}$ and greater than 30 g m$^{-2}$, respectively. This relocation can be attributed to the ongoing processes of re-suspension and sedimentation, naturally occurring in deep lakes resulting in the distinct erosion-transport-sedimentation zones as described by (Hakanson, 1977). The deep sediment (e.g. below 10 m water depth) may also be resuspended by wind driven water movements (Wetzel, 2001), whilst bioturbation (e.g. fish and chironomid larvae) may affect transport processes within a sediment. Collectively, these processes are likely to affect the distribution of the LMB within the sediment. With the result that not all LMB remains on the surface of the sediment after 3 years, as observed here (Fig. 3). A similar result was found by Dithmer et al. (2016b). Arguably, the sediment sample method (UWITEC core sample), may have relocated minor amounts of the LMB to deeper within the sediment, i.e. as the tube is forced into the sediment, friction between the tube and the sediment may cause small amounts of material forced downwards with the tube. Also, the effectiveness of the LMB may benefit from its redistribution.
towards the deeper sediments as most of the (labile) sedimentary P resides here (Oosterhout et al., 2019). Therefore, to ensure longevity of effectiveness dosing of the LMB should be based on an estimated communicating sediment depth, which is a difficult parameter to determine. In Lake Rauwbraken a communicating depth of 5 cm for FRP was assumed (Lürling and Oosterhout, 2013a), which was a fair estimate given the La as tracer measure in this study (Fig. 3) and in Dithmer et al. (2016b). This depth was estimated based on the bathymetry of the lake and paucity of bottom dwelling fish. However, if fish such as bream (Abramis brama) or carp (Cyprinus carpio) are present, their foraging behavior may substantially increase communicating sediment depths (Huser et al., 2016).

4.3. Sediment FLa release

FLa release after application was much higher than before (Table C.1). The hypothesis that FLa is not released from the sediment is rejected, which is consistent with the findings of Gibbs et al. (2011), who also found La release from the LMB. In the cores sampled in 2011 (3 years after application) the release of FLa was much lower. However, under anaerobic conditions, this release was an order of magnitude higher than under aerobic conditions: 0.063 versus 0.006 mg m⁻² day⁻¹, respectively. The hypothesis that the release of FLa is not affected by anaerobic-aerobic conditions is rejected. Based on the high binding capacity of La for FRP (Johannesson and Lyons, 1994; Liu and Byrne, 1997), and the fact that anaerobic conditions do not affect this, the differences in the release of FLa between aerobic and anaerobic conditions could be caused by ferrous iron ions displacing unconsolidated La from the clay interlayers and by methane ebullition under anaerobic conditions. The difference between the releases of FLa under aerobic and anaerobic conditions may result in seasonality in the lake FLa concentrations, i.e. as a result of thermal stratification. The highest mean FLa concentration was measured late in the year (mean FLa = 2.67 µg L⁻¹), the lowest early in the year (mean FLa = 1.36 µg L⁻¹; Table D.1). The highest FLa occurred in the deep layer during summer and late in the year (mean FLa = 3.18 µg L⁻¹ and 3.04 µg L⁻¹; Appendix D).

4.4. Macrophytes

The La associated with macrophytes increased. For the submerged macrophytes and the Nymphaea leaves it cannot be excluded that this increase is caused by LMB particles attached to the outside of the plants. For the emergent parts (stems) and inner tissues of the roots it is unlikely that this increase is caused by attached LMB. Thus, it is likely that La is taken up by macrophytes, this was also found by Yang et al. (1999) and Weltje et al. (2002). The La concentration in the inner tissues of the roots is higher than in the leaves.

The background La content in the submerged macrophyte Elodea nuttallii was 7.5 mg La kg⁻¹ DW, the same as has been found by Waajen et al. (2017b). Likewise, after the application La concentrations increased 235 to 389 times, while Waajen et al. (2017b) noted it increased 78 times, suggesting that La, either through bioaccumulation or attached LMB, becomes associated with macrophytes. This means that macrophytes can be a vector for La transfer to herbivorous fish and water birds. Earlier observations in Lake Het Groene Eiland (The Netherlands), treated with the LMB in 2008, revealed that after one year droppings of herbivorous birds, Canada Goose (Branta canadensis), contained between 0.03 and 69.5 µg La per g dry weight (median 0.4 µg La g⁻¹) (Lürling and van Oosterhout, 2013b). Thus, herbivorous birds may also be a vector for transport of La away from the treated location.

Evidently, macrophytes were not hampered by LMB or its active ingredient La as they massively expanded after the intervention. This is in line with reports on growth promotion and accelerated photosynthesis after exposure to La (Babula et al., 2008; Hong, 2005). At higher concentrations, La may cause negative effects on plants therewith expressing a typical hormetic dose response (Agathokleous et al., 2019). Given the chemistry of La (D’Haese et al., 2011), negative effects on rooted macrophytes are, however, not to be expected. Indeed, even at relatively high Phoslock dose in the sediment, up to 20% dry-weight, no adverse effects or growth inhibition was found (Wang et al., 2017). In Loch Fleming (UK), Phoslock led to improved growing conditions for macrophytes “without any noticeable negative impacts on the ecology of the aquatic macrophyte community” (Gunn et al., 2014). Field studies in general show increased macrophyte abundance and diversity after LMB applications (Spears et al., 2016; Waajen et al., 2016a, 2016b).

4.5. Chironomid larvae

With only one pre-application sample of chironomid larvae, it cannot be determined if the density of these larvae was changed after LMB application. However, some inferences can be made from densities of chironomids in similar season pre- and after intervention. These were similar or slightly elevated in the post-intervention period indicating no strong impact of the intervention (see Fig. 6A). The opposite was observed by Meis (2012) in the shallow Loch Fleming (UK), whereas in Lake De Kuil (The Netherlands) chironomids were absent before intervention, but appeared after (Waajen et al., 2017a).

La concentrations in the chironomid larvae post-application were several orders of magnitude higher than pre-application. Similarly, Waajen et al. (2017b) reported La concentrations of chironomid larvae over twice as high after LMB application than pre-application. The chironomid larvae were analyzed without gut cleaning and thus the elevated La concentrations may be due to direct ingestion.

The elevated La contents in the chironomids did not affect their P content that remained around 8.4 µg P mg⁻¹ DW (Fig. 7). Off course, part of this P might be biologically unavailable as bound to La, yet also in a controlled experiment with Chironomus sp. no detrimental effects were found with a marginal growth reduction at Phoslock capping dosing rate (Watson-Lung, 2005). Likewise, Clearwater (2004) tested in a 38 d chronic exposure test different doses of Phoslock (up to 400 mg L⁻¹) creating a 4–8 mm layer on
and Pennick, 2007, 2008). Indeed, La generally is considered to be strongly protein bound in the plasma (Damment et al., 2000). Animals in the food web – e.g. fish predating these larvae. Effects on chironomid larvae are not to be expected, the exposed sex ratio of the midge larvae. Studies in literature that La could be accumulated by the amphipod Corophium volutator (Lobel et al., 1991); in duckweeds (Spirulina polyrhiza), Cladocerans (Daphnia magna), goldfish (Carassius auratus L.), shellfish (Sinotaya Bellamya aeruginosa) (Yang et al., 1999) and carp (Cyprinus carpio) (Qiang et al., 1994). The uptake of La from the LMB becomes attached to the submerged macrophytes (Oosterhout et al., 2014). However, in none of those experiments the La speciation or any potential toxic effects were determined. Whilst the free La³⁺ cation carries the greatest risk of biological effects (Das et al., 1988), this ion will be virtually absent in eutrophic waters. There is also little evidence of La toxicity in humans as it is strongly protein bound in the plasma (Damment and Pennick, 2007, 2008). Indeed, La generally is considered to be of low toxicity, and depending on its chemical form, the acute oral dose of La as assessed in rats varies from 3400 mg kg⁻¹ to greater than 10,000 mg kg⁻¹ body weight (Redling, 2006). The absence of identifiable eco toxicity in whole lake applications (Waajen et al., 2016a; Waajen et al., 2017a) is therefore not surprising.

Lanthanum-based eutrophication management tools are powerful, since La precipitates with phosphate forming an extremely stable mineral in sediments (Dithmer et al., 2016b; Douglas, 1999, 2002), whilst it remains active until virtually all La has precipitated as rhabdophane without competition by other factors (Dithmer et al., 2016a). Consequently, the amount of phosphate that will be immobilized by the LMB can be calculated far more accurately than for other commonly used mitigation compounds, such as Al, which has Al:P binding ratios varying between 2:1 to 13:1 (Huser et al., 2011) and where floc ageing impairs the adsorption capacity (de Vicente et al., 2008), or phosphate bound to iron that can easily be released under anoxia or elevated pH (Søndergaard et al., 2003).

In 2013, 5 y after the treatment, the vast majority of the introduced La could be retrieved from the sediment, only a small fraction was lost to groundwater. The calculated amount of La in the sediment of the deep lake (619 kg) corresponds with an immobilization of 138 kg P. The improved water quality underpins that the introduced La has strongly reduced the internal P load in Lake Rauwbraken.

4.6 General

The rare earth element La can potentially be toxic to aquatic organisms depending on water composition. La concentration and its speciation (Akhurst et al., 2004; Barry and Meehan, 2000; Douglas et al., 2004, 2008; NICNAS, 2001). In hard water lakes and in eutrophic waters with elevated pH, however, virtually all FLa will be colloidal (Reitzel et al., 2017), because at higher alkalinity La precipitates with (bi)carbonate and at elevated pH insoluble La-hydroxide forms. In soft water lakes, Reitzel et al. (2017) showed that complexation of La with humic substances may occur. How much truly dissolved La³⁺ will be present depends on water chemistry, yet even if some trivalent ions are present, few detrimental effects of a LMB application on aquatic organisms are to be expected (D’Haeze et al., 2019).

The environmental safety of LMB is related to the low solubility (Ksp = 10⁻²⁴·² to 10⁻²⁵·⁷ mol² L⁻²) (Johannesson and Lyons, 1994; Liu and Byrne, 1997) of the La-PO₄ mineral (rhabdophane). The presence of La within the bentonite interlayers reduces the bioavailability and formation of FLa with bioavailability further reduced after binding with P. A review of LMB is given in (NICNAS, 2001), however, the bioavailability of La was not evaluated. There is evidence in literature that La could be accumulated by the amphipod Corophium volutator (Moermond et al., 2001), blue mussels (Mytilus edulis) (Lobel et al., 1991); in duckweeds (Spirulina polyrhiza), Cladocerans (Daphnia magna), goldfish (Carassius auratus L.), shellfish (Sinotaya Bellamya aeruginosa) (Yang et al., 1999) and carp (Cyprinus carpio) (Qiang et al., 1994). The uptake of La from the LMB has also been demonstrated in rainbow trout (Onchorhyncus mykiss) and koura (Paranephrops planifrons) (Landman et al., 2007), and the Marbled crayfish (Procambarus fallax f. virginalis) (Oosterhout et al., 2014). However, in none of those experiments the La speciation or any potential toxic effects were determined. Whilst the free La³⁺ cation carries the greatest risk of biological effects (Das et al., 1988), this ion will be virtually absent in eutrophic waters. There is also little evidence of La toxicity in humans as it is strongly protein bound in the plasma (Damment and Pennick, 2007, 2008). Indeed, La generally is considered to be of low toxicity, and depending on its chemical form, the acute oral dose of La as assessed in rats varies from 3400 mg kg⁻¹ to greater than 10,000 mg kg⁻¹ body weight (Redling, 2006). The absence of identifiable eco toxicity in whole lake applications (Waajen et al., 2016a; Waajen et al., 2017a) is therefore not surprising.

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5. Conclusions

Lanthanum was present at low concentrations in sediment, water column, macrophytes, and chironomid larvae before the LMB application. After the application of the LMB, both filterable and total lanthanum in the water column were elevated and remained so as compared to the pre-application concentrations.

While immediately after the application, FLa and TLa concentrations in the water column exceeded maximum permissible concentrations as defined for the Netherlands, they did return to below these maximum permissible concentrations after 11 weeks after application for FLa and 2 weeks for TLa. It should be noted, however, that the Dutch La standards are based on a single experiment that contains a methodological flaw.

The LMB was distributed homogeneously over the lake bottom during its application. Three years after the application, the LMB was redistributed from shallow zones to greater depths.

Lanthanum from the LMB was taken up by submerged macrophytes. The LMB becomes attached to the submerged macrophytes and is present in the gut concentration of chironomid larvae. Meaning that submerged macrophytes and chironomid larvae may be a vector for La in the food chain.

Sediment core studies revealed that anoxic conditions may increase La release into the overlying water column. The precise mechanisms is as yet undetermined and requires further investigation.

Lanthanum concentrations in filtered samples depend on pore size of the filter suggesting that various colloidal forms of La are present. The implication is that the true concentration of FLa may be lower than previously estimated. The seasonality in FLa and TLa needs further investigation.

The dimensions of the sediment traps as deployed in our study to sample massive sedimentation events such as a LMB application need to be reconsidered.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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Appendix A. Supplementary data

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