Responses in sediment phosphorus and lanthanum concentrations and composition across 10 lakes following applications of lanthanum modified bentonite

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ABSTRACT

A combined field and laboratory scale study of 10 European lakes treated between 2006 and 2013 with a lanthanum (La) modified bentonite (LMB) to control sediment phosphorus (P) release was conducted. The study followed the responses in sediment characteristics including La and P fractions and binding forms, P adsorption capacity of discrete sediment layers, and pore water P concentrations. Lanthanum phosphate mineral phases were confirmed by solid state ^{31}P MAS NMR and L_{III} EXAFS spectroscopy. Rhabdophane ($LaPO_4 \cdot nH_2O$) was the major phase although indications of monazite ($LaPO_4$) formation were also reported, in the earliest treated lake. Molar ratios between La and P in the sediments were generally above 1, demonstrating excess La relative to P. Lanthanum was vertically mixed in the sediment down to a depth of 10 cm for eight of the ten lakes, and recovery of La in excess of 100% of the theoretical aerial load indicated translocation of the LMB towards the deepest areas of the lakes. Lanthanum was generally recovered from bed sediment samples following sequential chemical extraction from the HCl fraction. Soluble reactive P (SRP) release experiments on intact sediment cores indicated conditions of P retention (with the exception of two lakes) by sediments, indicating effective control of sediment P release, i.e. between two and nine years after treatment.

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1. Introduction

Eutrophication of freshwaters is a global problem caused mainly by elevated phosphorus (P) concentrations in the sediment due to P emissions from agriculture and sewage. Control and regulation of these emissions have improved significantly in recent years, in order to fulfil legislation on water quality, such as the European Water Framework Directive (European Union, 2000). However, the release of legacy stores of P in lake bed sediments can confound catchment management by maintaining elevated water column TP concentrations for decades and may also need to be controlled.

Chemical lake restoration, also referred to as geo-engineering, has been demonstrated as a measure for controlling sediment P release resulting in rapid chemical recovery following catchment management (Mackay et al., 2014; Spears et al., 2014). To date, chemicals including iron (Fe) and aluminium (Al) in the form of oxides and hydroxides have been widely used for P control in lakes (Boers et al., 1992; Cooke et al., 1993; Welch and Schrieve, 1994; Welch and Cooke, 1999; Lewandowski et al., 2003; Reitzel et al., 2005) but engineered materials like the lanthanum-modified bentonite Phoslock® (LMB) (Douglas et al., 1999; 2002; Copetti et al., this issue) have received increasing attention in recent years. Most published literature on LMB has focused on laboratory or mesocosm studies (Egemose et al., 2010; Reitzel et al., 2012, 2013; Bishop et al., 2014; Lürling et al., 2014), with assessment of chemical and

ecological responses of LMB treated lakes being relatively rare (van Oosterhout and Lürling, 2011; Meis et al., 2012; Crosa et al., 2013; Spears et al., this issue). Spears et al. (2013a and this issue) demonstrated the importance of considering field scale responses following applications across multiple treated lakes, providing evidence to support laboratory based trials.

In general, laboratory studies on LMB have included studies concerning either toxicity or P binding efficiency of LMB (Copetti et al., this issue). Toxicity studies have shown that La accumulates in organisms (e.g. crayfish) but without noticeable side-effects (van Oosterhout et al., 2014), and does not appear to limit the growth of aquatic macrophytes in the field (Gunn et al., 2014; Spears et al., this issue; Copetti et al., this issue). Studies on the efficiency of LMB performed under different environmental conditions have shown that at pH above 8.5 interference with the binding of soluble reactive phosphorus (SRP) to LMB can occur (Ross et al., 2008; Vopel et al., 2008; Egemose et al., 2010; Gibbs et al., 2011; Reitzel et al., 2013). Moreover, under low alkalinity conditions dispersion of the clay matrix can result in higher concentrations of La in the lake water (Spears et al., 2013a), but also an improved SRP binding capacity (Reitzel et al., 2013). Elevated concentrations of dissolved organic carbon (DOC) in the water column appear to reduce the SRP binding performance of LMB over short time scales by reducing the formation of the La phosphate, as demonstrated by Lürling et al. (2014) and Dithmer et al. (this issue). However, a negative impact of DOC on binding performance appears to be overcome with time (Dithmer et al., this issue). In general, these observations suggest lower than expected P control by LMB in full scale treatments, when compared to theoretical binding capacity used to estimate product dose (i.e. 1 tonne LMB to control 11 kg P).

Knowledge on the performance of LMB in bed sediments under natural conditions is limited (Meis et al., 2012, 2013). We address this knowledge gap by examining the behaviour of LMB and its interactions with phosphate and other substances present in the bed sediments across 10 treated lakes (Table 1). Specific La phosphate mineral formation is assessed (using extended x-ray absorption fine spectroscopy (L_{III} EXAFS) and solid state ^{31}P MAS NMR) within bed sediments of treated lakes to determine that La and P had precipitated as Rhabdophane ($LaPO_4 \cdot nH_2O$). Sediment profiles of both La and P were constructed to determine vertical sediment mixing of La following LMB applications, to test the hypothesis that LMB will be vertically and horizontally mobile in bed sediments following application. Finally, to determine the operational performance of the LMB treatments, we quantified SRP efflux from intact sediment cores, the P binding capacity of bed sediments, and La and P composition across operationally defined sediment P pools using a standard sequential chemical extraction procedure. The implications of these results for the wider application of LMB are discussed.

2. Methods and materials

2.1. Study sites and sample collection

Ten lakes; United Kingdom (UK) (2), Germany (DE) (5), and the Netherlands (NL) (3), treated between November 2006 and March 2013 with LMB, were sampled in June 2014. The treatments were performed with LMB applied as slurry from a boat or barge to all lakes; however small variations in the treatment procedures including the use of low doses of flocculants were conducted in some cases (Table 1).

Sediment cores were collected from a boat at the deepest part of each lake (12 cores for each UK lake and 11 cores for each of the Dutch and German lakes) with a Kajak gravity corer (Ø = 5.2 cm), with the exception of Lake Blankensee, where the sampling was conducted at a fixed sampling spot with a depth of 1.5 m. Epilimnetic lake waters were sampled, and following filtration (cellulose acetate membrane filter 0.45 μm), alkalinity (Gran Plot titration), dissolved organic carbon (DOC; infrared spectrophotometric analysis using a Shimadzu TOC 5000 Total organic carbon

Table 1
General data for the LMB treated lakes in Germany (DE), United Kingdom (UK) and the Netherlands (NL). Additional treatment beyond a single LMB addition is noted together with alkalinity (mmol L^{-1}), DOC (mg L^{-1}), summer average TP (μg L^{-1}, (std)), and Chl. A. (μg L^{-1}, (std)) measured in the epilimnion. The dose of LMB to each lake is shown in Table 3.

Lake	Place	Date	Additional treatments	Area (ha)	Depth mean (m)	Alk (mmol L^{-1})	DOC (mg L^{-1})	TP$_{pre}$ (μg L^{-1})	TP$_{post}$ (μg L^{-1})	Chl. A.$_{pre}$ (μg L^{-1})	Chl. A.$_{post}$ (μg L^{-1})
Otterstedter See	DE	nov-06	Hypolimnetic withdrawl	4.5	5.0	0.8	9.6	59[1]	35(2)[11]	n/a	n/a
Silbersee	DE	nov-06	Hypolimnetic withdrawl[+]	7.0	5.0	1.6	4.3	150[2]	158(4)[11]	n/a	n/a
Rauwbraken	NL	mar-08	Flocculent (PAC)[a,b]	2.6	8.8	0.4	4.7	133(143)[3]	15 (13)1[12]	28 (85)[3]	4 (6)[12]
H. G. Eiland	NL	apr-08		5.0	2.5	2.0	2.8	32 (26)[4]	29 (26)[13]	n/a	n/a
Kuil	NL	apr-09	Flocculent (FeCl$_3$)*	6.7	4.0	2.8	9.2	72 (126)[5]	12 (6)[14]	22 (28)[5]	5 (3)[14]
Blankensee	DE	dec-09		22.5	1.6	0.8	8.6	10[6]	n/a	38[6]	n/a
Behlendorfer See	DE	dec-09	None*	64.0	6.2	1.6	9.3	110[7]	n/a	26[7]	n/a
Eichbaumsee	DE	nov-10	Flocculent (PAC)[b]	23.2	6.5	2.5	5.9	358[8]	91[15]	32[8]	28[18]
Mere Mere[c]	UK	mar-13		15.8	2.8	1.3	14.4	77[16]	75[17]	16[16]	13[17]
Hatchmere[c]	UK	mar-13		4.7	1.4	2.0	16.7	83[16]	73[17]	18[16]	32[17]

[a] Lürling and van Oosterhout (2013a, b).
[b] PAC (polyaluminumchloride).
[c] Spears et al. (2013a).
*Uneven distribution of LMB, all (Lake Behlendorfer) or majority (Lake Kuil) applied directly at deepest spot. [a]Hypolimnetic withdrawal for four months in summer 2005 [+]Hypolimnetic withdrawal for seven month in summer seasons between 2003 and 2005. In total 18 kg P was removed, [b]Replicate additions. [1]2005–2006, [2]2006, [3]2006–2007, [4]2008–2010 (untreated lake area), [5]2000–2008, [6]2009, [7]2008, [8]2004–2010, [11]SRP measured at the time of our sampling campaign, [12]2008–2014, [13]2008–2010 (treated lake area), [14]2009–2014, [15]2011, [16]mean of 12 months before application, [17]mean of 12 months following application.
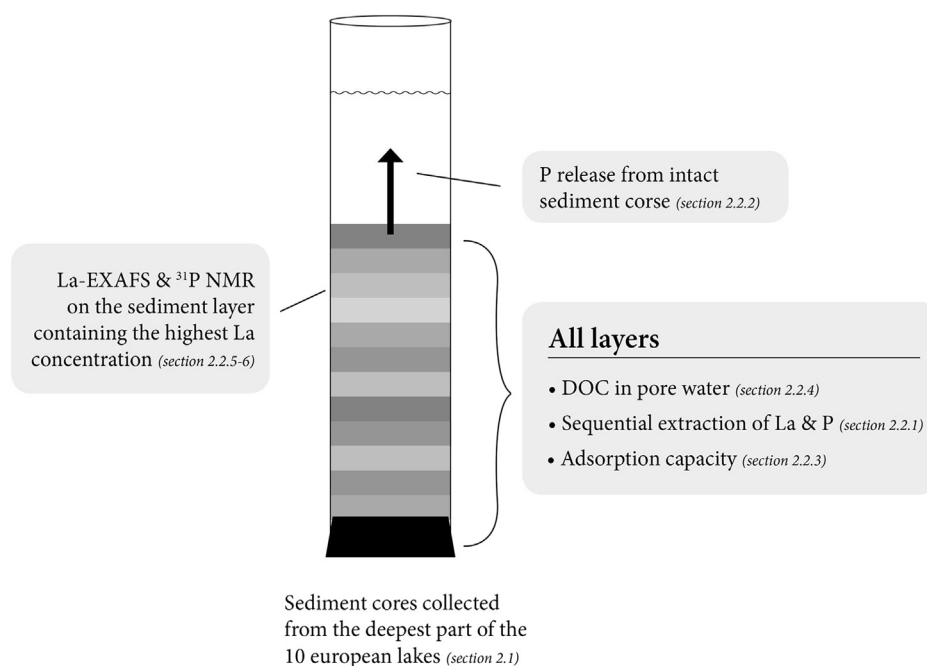
Fig. 1. Overview of the analysis performed on the sediment cores from the ten lakes.

analyser) and SRP concentrations (spectrophotometric analysis; Koroleff, 1983) were determined. In Fig. 1, the various analyses performed on the sediment are shown.

On collection, three sediment cores were sectioned for sequential P and La extraction. The upper 10 cm of the sediment cores were sliced in one cm intervals and identical sediment depth layers from each of the three cores were pooled into one composite sample. An exception was made for Lake Otterstedter See and Lake Blankensee, where the upper 6 cm and 3 cm were pooled, respectively, and the following 10 cm were sliced in 1 cm thicknesses, upon request from the lake managers. Four additional cores were sectioned as above and samples were pooled in zipper storage bags for SRP sorption experiments, pore water analysis of DOC and ^{31}P MAS NMR and La L[III] EXAFS spectroscopy. Furthermore, four (NL, DE) or five (UK) intact sediment cores were brought back to the lab and used for the SRP flux experiment (section 2.2.2.).

From the pooled sediment samples, approximately 5 g subsamples were removed, dried at ambient temperature and used for the determination of total La (TLa) and total P (TP) concentrations using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Optima 2100 DV, Perkin Elmer (standard deviation on replicate samples of less than 2%). Following this analysis, the sediment depth sample with the highest TLa concentration was used for ^{31}P MAS NMR and L[III] EXAFS analyses. Dry weight (DW) was determined by drying sediment at 105 °C for 24 h and loss on ignition (LOI) by combusting subsamples of the dried sediment for 5 h at 520 °C.

2.2. Sediment analysis

2.2.1. Vertical distribution of La and P pools in the sediment

Fresh sediment (1.0 g) from each pooled sediment sample was sacrificed for the determination of operationally defined sediment P pools using a modified chemical extraction procedure (Reitzel, 2005). The TLa and TP concentrations recovered following sequential extractions in water (H_2O), bicarbonate dithionite ($HCO_3^-/S_2O_4^{2-}$; BD), sodium hydroxide (NaOH), hydrochloric acid (HCl) and residual (Res) were determined using ICP-OES. Total La and TP analyses were performed on subsamples of the pooled sediment following addition of concentrated nitric acid (HNO_3) and combustion in a microwave oven for 15 min prior to analysis by ICP-OES. Sediment densities in the respective layers were calculated and used to express the amount of La and P per unit surface area of sediment (expressed as mmol m^{-2}).

Generally, the HCl treatment is known to extract calcium phosphates from sediments (e.g. Reitzel, 2005). In addition, previous studies have shown that most of the La bound P is recovered in the HCl extract (Meis et al., 2012; Reitzel et al., 2013). Hence, the La:P binding ratio in the HCl extracts can be used to evaluate whether all the La sites of the LMB are binding P. Given the lack of pre-application data available from the studied lakes on sediment P properties it was assumed that the HCl-P concentrations in the LMB treated sediment at depths where the HCl-La concentration approached zero represented background HCl-P conditions, further assuming a uniform background concentration of HCl-P throughout the sediment profile, as seen in e.g. Jensen and Thamdrup 1993 and Reitzel et al., 2005. The total amount of La phosphate as a result of the LMB treatment was estimated by subtracting the background HCl-P amounts from the amount of HCl-P in the sediment layers containing La. This procedure was used for Lake Rauwbraken, Lake Blankensee, Lake Het Groene Eiland, Lake Behlendorfer See, Lake Eichbaumsee and Hatchmere. For the remaining lakes the HCl fraction of all layers contained La. Consequently, it was assumed that all the HCl-P solely reflected La phosphate, which most likely overestimates the La phosphate content in sediment layers of these lakes.

2.2.2. SRP flux experiments on intact sediment cores

The SRP flux across the sediment-water interface was measured at room temperature (20 °C) in either four (NL, DE) or five (UK) replicate intact sediment cores incubated for 22−30 h under oxic conditions (i.e. no lid on the cores), corresponding to the natural conditions in the lake, at the time of sampling. Samples for SRP concentrations were collected from the water overlying the

sediment in each core at the beginning and at the end of the incubation periods. The SRP concentrations were related to water volume and surface area in the sediment cores to express SRP flux per unit area per day (mmol m^{-2} d^{-1}).

2.2.3. SRP adsorption experiments

The SRP binding capacity of each sediment layer was determined by suspending 1 g fresh sediment (n = 3) from each layer of the pooled sediment (from four cores, see section 2.1) in 40 mL purified water containing 1.98 mg L^{-1} SRP added as K$_2$HPO$_4$, with pH adjusted to 6.5 using NaOH. Soluble reactive P concentrations were measured before and after incubation for approx. 24 h on a shaking table, followed by separation of sediment and solution by centrifugation (10 min, RCF = 1200), filtration of the supernatant (cellulose acetate membrane filter 0.45 μm) and acidification of the filtrate (2 M sulphuric acid).

2.2.4. Pore water analysis

Pore water DOC concentrations were determined following collection of 4 mL of pore water from each of the composite sediment samples after centrifugation (10 min, RCF 1200) and filtration (cellulose acetate membrane filter0.45 μm).

2.2.5. Solid state ^{31}P MAS NMR

Solid state ^{31}P MAS NMR spectra were obtained for the sediment layer containing the highest La concentrations from each lake. The measurements were conducted on a Varian INOVA 500 MHz instrument with a spinning speed of 10 kHz, 8 s relaxation time and 5000 or 10,000 scans depending on the TP concentration. The ^{31}P MAS NMR spectra were deconvoluted using SpinWorks 3.1.8.1 (Marat, 2011).

2.2.6. L$_{III}$-EXAFS

To study La phases in the sediment EXAFS measurements were performed at beamline I811, MAX-lab, Lund University, Sweden, which operated at 1.5 GeV and a current of 250 mA. The X-ray beam was detuned to minimize higher-order harmonics, and data were obtained in fluorescence mode with a PIPS detector. Five consecutive scans of 180 s were measured at the La L$_{III}$-edge (5483 eV) of finely ground sediment samples from the layer containing the highest La concentration from each lake.

In all spectra, double electron excitations were observed, an anomalous feature common in EXAFS for lanthanides (Solera et al., 1995; Ohta et al., 2008). This was removed with built-in functions in EXAFSPAK (George and Pickering, 2000). In addition, the Barium (Ba) L$_{II}$-edge (at 5624 eV) was observed. This interference is caused by the Ba content in the LMB (620 μg Ba g^{-1} DW (Spears et al., 2013b)), naturally occurring Ba in the bed sediments (e.g. 5—600 μg Ba g^{-1} DW in Clatto Reservoir, UK (Meis et al., 2012)) or both. A pre-treatment sediment sample from Loch Flemington, UK, was used as reference to counteract for this interference, by performing a baseline subtraction of a linearly scaled background measurement with a strong Ba L$_{II}$ peak, effectively removing the interfering Ba peak without affecting the rest of the data set. Data treatment was performed in EXAFSPAK and afterwards fitted with scattering paths obtained with FEFF 7.02 (Zabinsky et al., 1995). The data were analysed using refinement of single-scattering La-O distances, and the distances for pure synthesized rhabdophane (LaPO$_4$ · H$_2$O) is 2.47(1) Å and for monazite (LaPO$_4$) 2.52(1) Å (Dithmer et al., 2015a) were used as initial distances. Additional scattering pathways (La—P, La—O—P, La—C, La—O—C) were included with fixed average distances determined from ICDD and FEFF-calculations, and not refined due to the complexity of the EXAFS data.

2.3. Statistical analyses

Pearson's correlations were performed to allow examination of responses and potential drivers operating across the studied lakes. Only relevant significant (p < 0.05) correlations are reported. The statistical analysis was performed using SigmaPlot 12, Systat Software Inc.

3. Results

3.1. Vertical distribution of La and P in the sediment

In general, the HCl extract contained the largest fraction of La, whereas the distribution of P across operational fractions was more diverse (Fig. 2). HCl extractable La and HCl extractable P were generally mixed across the upper 10 cm of the sediment (and for some lakes even below this depth) except for Lake Rauwbraken, Lake Eichbaumsee and to a lesser extent, Hatchmere, where distinct La and P profiles were observed to increase towards the surface (Fig. 3). Between 60% and 98% of TLa was recovered following sequential extraction, and there was a significant (p < 0.05) positive correlation between unrecovered La and unrecovered P (Pearson's r = 0.61, R^2 = 0.38), indicating a general loss of material during the extraction procedure.

Total La (mmol m^{-2}) calculated from the sliced sediment cores (see 2.2.1) was determined as well as an estimate of the theoretical mass of La applied per m^2 (4.5 w/w% La in the LMB) (Table 2). The applied La dose varied between 71 and 228 mmol La m^{-2} and the overall recovery of La at the deepest site was 87% for Lake Otterstedter See, 95% for Lake Blankensee, and 60% for Lake Behlendorfer See, whereas the recovery in the remaining seven lakes was between 146 and 296%.

The estimated HCl extractable La:P ratio (section 2.2.1) varied between 0.4 in Lake Silbersee to 4.5 in Lake Het Groene Eiland (Table 2). For some lakes positive significant (p < 0.05) correlations were reported between the accumulated concentrations of HCl-La and HCl-P, HCl-La and Res-La, HCl-La to TLa (Table 3).

3.2. Depth dependent sediment adsorption capacity

The SRP adsorption capacity of the sediments (μg SRP g DW^{-1}d^{-1}) generally decreased with increasing depth in all lakes (Fig. 4) and there were no significant positive correlations between the SRP adsorption capacities and TLa, with the exception of Lake Otterstedter See (Pearson's r = 0.67, R^2 = 0.44) and Hatchmere (Pearson's r = 0.66, R^2 = 0.43).

3.3. SRP flux experiments on intact sediment cores

The sediment SRP efflux was close to zero for eight of the lakes (Hatchmere, Mere Mere, Lake Rauwbraken, Lake Kuil, Lake Silbersee, Lake Behlendorfer See, Lake Otterstedter See, and Lake Eichbaumsee; range of −1.6 ± 6.0 to 0.3 ± 5.1 mg SRP m^{-2} d^{-1}) (Table 4). Lake Het Groene Eiland (10.8 ± 11.5 mg SRP m^{-2} d^{-1}) and Lake Blankensee (9.2 ± 4.6 mg SRP m^{-2} d^{-1}) had an efflux of SRP from the sediments to the water column.

3.4. Pore water analysis

Pore water DOC concentrations in Lake Het Groene Eiland were below 6 mg DOC L^{-1} for all sediment layers, whereas concentrations in Lake Otterstedter See, Hatchmere, and Lake Rauwbraken were all above 15 mg L^{-1}, with the remaining six lakes ranging between 5 and 15 mg L^{-1} (Fig. 4).
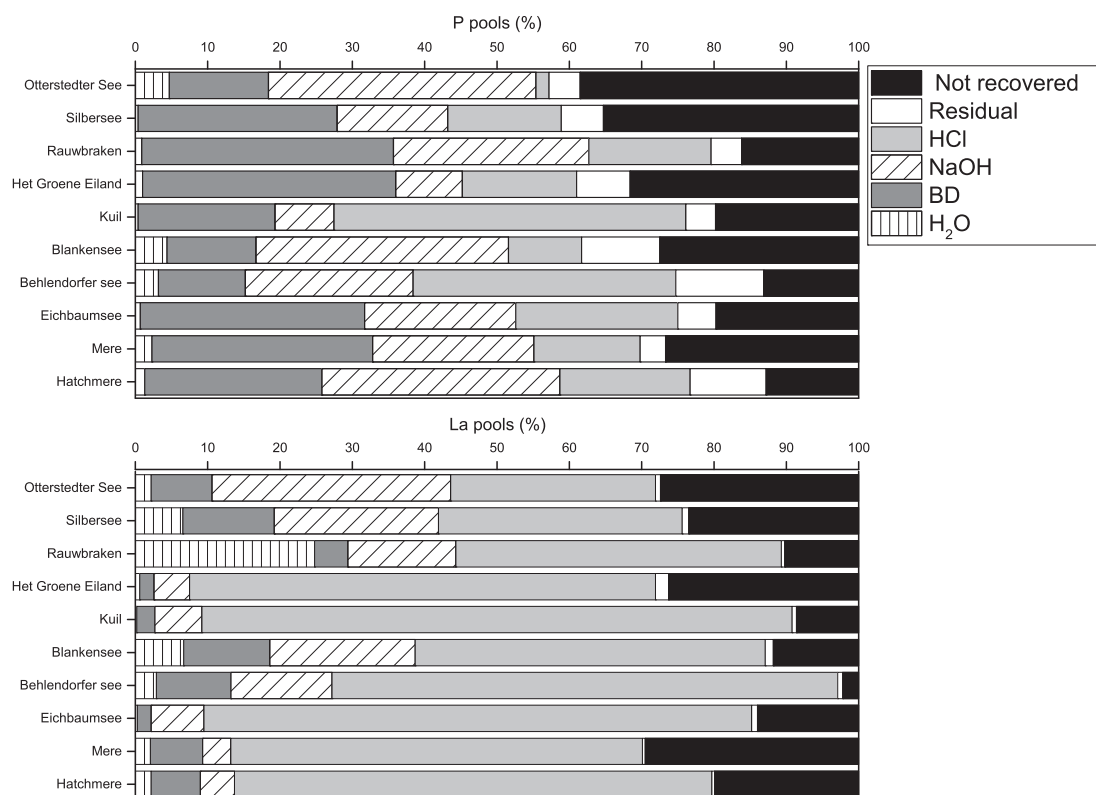
Fig. 2. The distribution (%) of TLa and TP in the various accumulated (upper 10 cm) fractions from a sequential extraction: H_2O-, BD-, NaOH-, HCl-, residual and the un-recovered fractions.

3.5. La and P binding forms identified by ^{31}P MAS NMR and EXAFS

3.5.1. ^{31}P MAS NMR spectroscopy

The sediment depth layer with the highest La concentration from each lake was analysed by ^{31}P NMR to determine the P forms in the treated sediment. Rhabdophane ($LaPO_4 \cdot n\ H_2O$) was identified in all samples and characterized by an isotropic chemical shift, δ_{iso}, of $-3.1(1)$ to $-3.9(5)$ ppm, with the exception of Lake Otterstedter See ($\delta_{iso} = -4.5(1)$ ppm) which was assigned to monazite ($LaPO_4$; Table 5; Figure SI-1). The chemical shifts assigned to rhabdophane varied slightly compared to rhabdophane in pure LMB samples (Dithmer et al., 2015a), which is explained by interference from external factors such as e.g. Fe in the sediment causing a small downfield shift. The second relevant P-species identified was assigned to hydroxyapatite ($Ca_{10}(PO_4)_3(OH)$), with a chemical shift at $1.5(5)-2.5(3)$ ppm (Shand et al., 1999; Cade-Menun, 2005; Dougherty et al., 2005) and constituted $20-60\%$ of the total intensity (Table 5). Phosphate species adsorbed to the surface of rhabdophane were expected (Dithmer et al., 2015a), but the position of this resonance ($\delta_{iso} = -0.48$ ppm, Dithmer et al., 2015a) is between that of hydroxyapatite and bulk rhabdophane. Thus, it is masked by the broadness of the spectra.

3.5.2. La L_{III}-EXAFS

The sediment samples from the ^{31}P NMR study were also analysed by EXAFS (Table 5). The bond-distances, d_{La-O}, were determined from extracted k^3-weighted $X(k)$ functions and the corresponding Fourier Transforms (Figure SI-2). The distances were assigned to be representative for rhabdophane, except in Lake Behlendorfer See (2.51(1) Å) and Lake Blankensee 2.56(1) Å), which were assigned to either monazite or a mixture of rhabdophane, monazite and unreacted La in the clay matrix, as previously

observed by Dithmer et al. (2015a). The La concentrations in sediment samples from Lakes Silbersee and Het Groene Eiland were too low for a reliable analysis of the EXAFS data.

4. Discussion

This study demonstrated that LMB treatment of the ten lakes resulted in the sequestration of P in the form of rhabdophane. In addition, LMB was generally mixed vertically in the sediments at the deepest area of the lakes, which may have resulted in reduced P removal efficiency at the sediment water interface at the whole lake scale, depending on the depth of the sediment layer that interacts with the water body. However, at the sampling stations, the lakes generally had a low SRP sediment efflux at the time of sampling indicating that LMB, or other P binding properties of the bed sediments, controlled the release of P across the sediment-water interface. The La:P ratios in the sediments were generally above 1, which indicates that not all La had reacted with P yet. However, these La containing layers did not display any increased SRP binding capacity. These two observations indicate there is no unreacted La available for additional sequestration of P.

4.1. Speciation of La and P in the sediment

The sequential La and P extractions showed that the majority of TLa and TP were recovered following HCl extraction, in agreement with earlier findings by Meis et al. (2012) and Reitzel et al. (2013), and in agreement with the fact that HCl is generally known to dissolve mineral phases. This is further supported by the ^{31}P NMR EXAFS results which demonstrated that the main La phosphate formed was rhabdophane. The only exception was Lake Otterstedter See where 45% of the La was recovered following NaOH
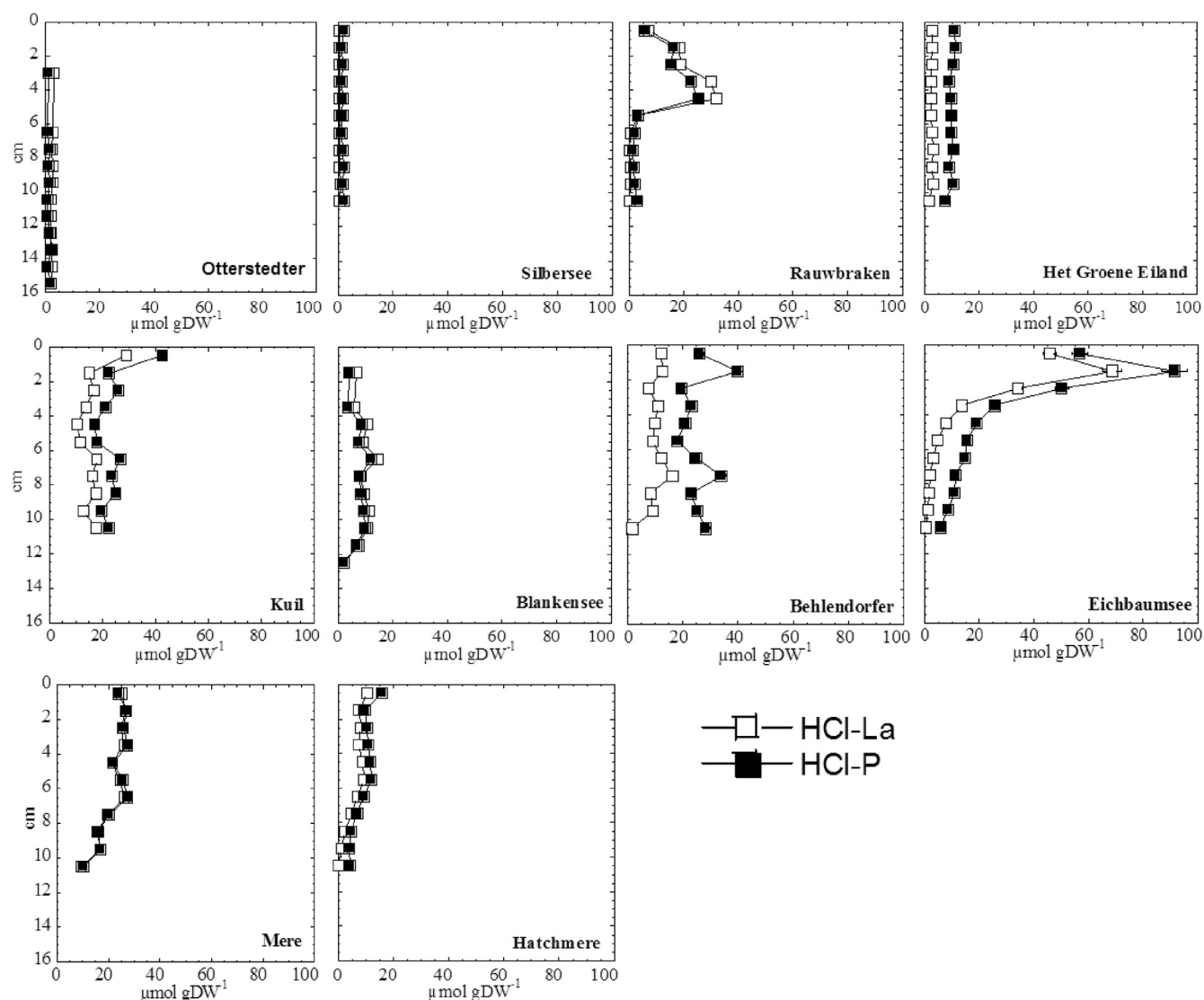
Fig. 3. The HCl-extractable content of La (white) and P (black) in the sediment profile of the ten LMB treated lakes.

Table 2
The molar ratio in the HCl-fraction calculated from the accumulated concentrations (mmol m^{-2}) from a sequential extraction. The applied amount of La is calculated based on the dose of LMB and the lake area and the percentages recovery of TLa. Standard deviations are shown in brackets.

Lake	HCl La:P	La applied mmol m^{-2}	TLa recovery%
Otterstedter	1.8(0)	79	87(1)
Silbersee	0.4(0)	99	146(1)
Rauwbraken	1.4(2)	228	195(2)
H. G. Eiland	4.5(1)	71	266(4)
Kuil	0.7(4)	201	142(8)
Blankensee	1.2(0)	95	95(1)
Behlendorfer	1.1(0)	186	60(2)
Eichbaumsee	0.9(2)	207	174(4)
Mere Mere	1.0(2)	164	296(2)
Hatchmere	1.6(2)	174	278(6)

extraction and 39% of the La was recovered following HCl fraction. This may be due to complexation of La and organic matter extracted by the NaOH solution (e.g. Reitzel et al., 2005).

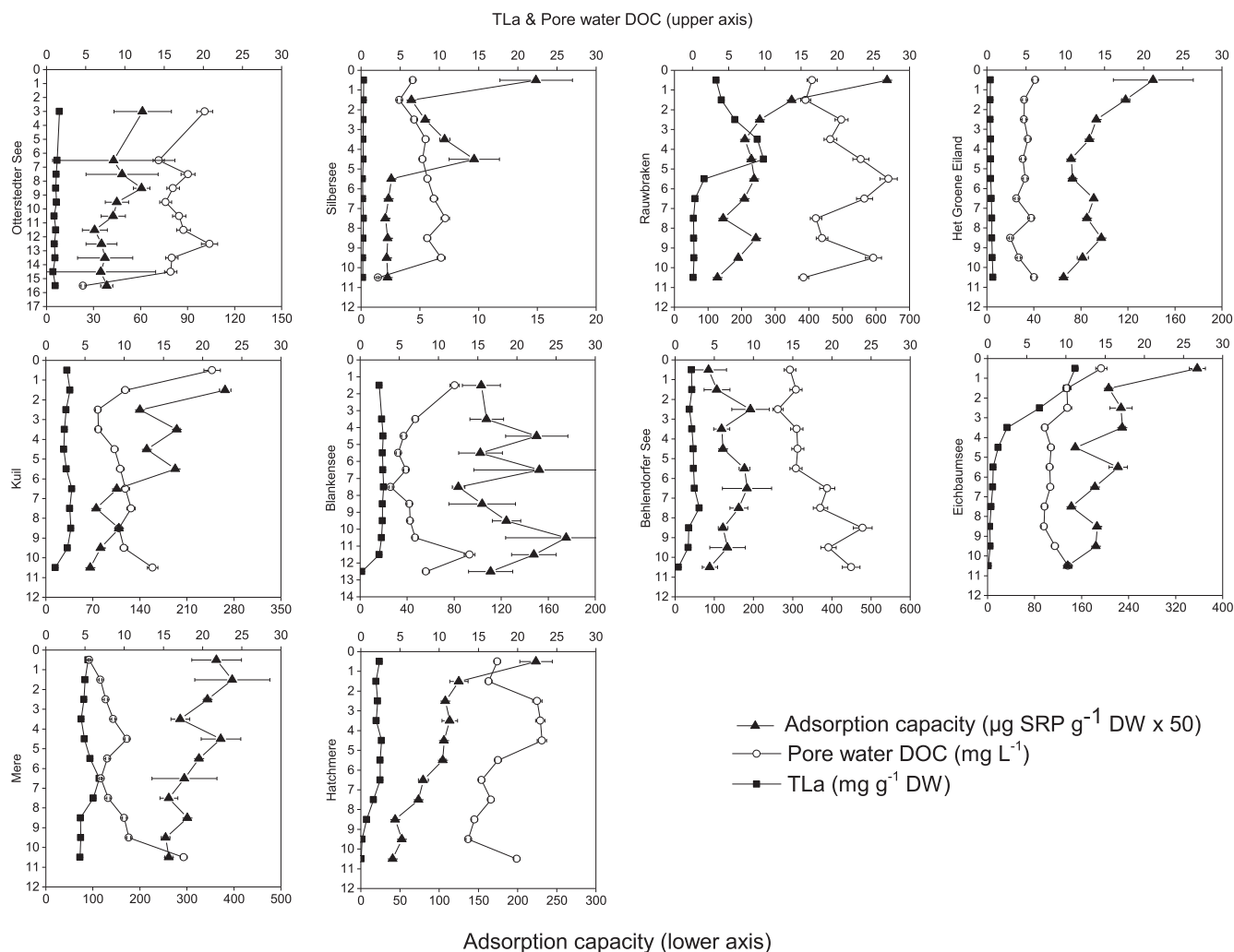Residual-La constituted up to 60% of the HCl-La fraction in a Danish eutrophic lake sediment manipulated under laboratory-controlled conditions (Reitzel et al., 2012). However, a significant positive correlation was observed between the HCl-La and Res-La concentrations. A possible explanation for this is that the HCl extraction does not extract all La in the samples during the extraction time used (1 h followed by a 5 min extraction). Hence, the second extraction time may be too short to extract all La. Alternatively, carbonates present in the clay matrix may lower the extraction efficiency of the HCl solution. This agrees well with the observation that the highest Res-La content was observed for the three lakes with highest alkalinity (Lake Het Groene Eiland, Lake Kuil and Lake Eichbaumsee).

4.2. Vertical distribution of La in the sediment

The vertical distribution of La was generally uniform for the sediment depths sampled across the lakes, indicating a rapid translocation from surface sediments to deeper sediment layers. This is in agreement with Meis et al. (2012, 2013), and Reitzel et al. (2012). However, the depths of distribution reported in this study were more than double that reported by Reitzel et al. (2012). For eight lakes, vertical mixing of LMB is probably the result of

Table 3
Pearson's correlation matrix. Number in brackets denotes the correlation value ($p < 0.05$).

	Res-La	T La	HCl-P
HCl-La	Otterstedter (0.84)	Rauwbraken (1.0)	Silbersee (0.79)
	Silbersee (0.96)	Kuil (0.65)	Rauwbraken (0.99)
	Rauwbraken (0.99)	Blankensee (0.81)	HG Eiland (0.85)
	HG Eiland (0.93)	Behlendorfer (0.95)	Kuil (0.99)
	Kuil (0.97)	Eichbaum (0.96)	Blankensee (0.97)
	Behlendorfer (0.76)	Hatchmere (0.96)	Eichbaum (0.99)
	Eichbaum (0.93)		Mere (0.99)
	Mere (0.89)		Hatchmere (0.87)
	Hatchmere (0.98)		

TLa & Pore water DOC (upper axis)

Adsorption capacity (µg SRP g^{-1} DW x 50)
Pore water DOC (mg L^{-1})
TLa (mg g^{-1} DW)

Adsorption capacity (lower axis)

Fig. 4. Total La content and pore water DOC concentration (upper axis) and adsorption capacity (lower axis) in the sediment profile for ten lakes. Note different scales on the lower x-axis (adsorption capacity).

bioturbation by animals such as chironomids (as shown by Reitzel et al., 2012), sediment mixing behaviour of bottom feeding fish such as bream (Breukelaar et al., 1994) or wind driven sediment resuspension (Egemose et al., 2010). These factors seem to play a minor role in Lake Rauwbraken and Lake Eichbaumsee, where distinct La and P profiles were observed. We did not observe any correlation between time since application of LMB and vertical mixing of the sediment, probably because the sediment mixing is an ongoing process that will quickly redistribute the sediment. Neither did we observe a trend between the degree of mixing and effectiveness of LMB treatment evaluated by either sediment SRP efflux or post treatment TP concentrations in the water.

The recovery of TLa from the sediment was in excess of 100% of the theoretical product dose for seven of the ten lakes. Sediment focusing of LMB towards the deepest areas of the lakes could be responsible for this phenomenon (Hilton, 1985) where shallow water sediments are continually disturbed and transported to deeper water sediment zones. This accumulation of La at the deepest sites could also explain the generally low SRP release observed from the sites in this experiment, and might not give a reliable picture of the sediment P release at the whole lake scale. This observation may also be explained by variation in the product application procedures. For example, the application of LMB to Lake Kuil and Lake Behlendorfer See were purposefully uneven, the

Table 4
SRP release and standard deviations from intact sediment cores collected in the ten LMB treated lakes.

Lake	SRP release (mg P·m^{-2}·d^{-1})
Otterstedter	0.2 ± 4.1
Silbersee	0.1 ± 2.8
Rauwbraken	−0.7 ± 4.7
H. G. Eiland	10.8 ± 11.5
Kuil	0.3 ± 5.1
Blankensee	9.2 ± 4.6
Behlendorfer	1.1 ± 13.8
Eichbaumsee	−1.6 ± 6.0
Mere Mere	0.0 ± 1.4
Hatchmere	−0.2 ± 0.4

Table 5
The results from the ^{31}P NMR and EXAFS analyses. Standard deviations shown in brackets.

Lake	^{31}P NMR				EXAFS
	δ_{iso} (ppm)[a]	I (%)[a]	δ_{iso} (ppm)[b]	I (%)[b]	d_{La-O} (Å)
Otterstedter See	−4.5(1)	62(2)	−11.5(4)	38(2)[c]	2.44(1)
Silbersee	−3.1(1)	56(4)	2.6(3)	44(4)	n.d.
De Rauwbraken 4-5	−3.4(2)	82(2)	2.0(9)	18(2)	2.49(1)
Het Groene Eiland	−3.9(5)	38(1)	1.9(2)	62(7)	n.d.
De Kuil	−3.5(3)	54(1)	2.0(4)	46(1)	2.47(1)
Blankensee	−3.5(1)	76(7)	2.1(2)	24(7)	2.56(1)
Behlendorfer See	−3.7(3)	52(8)	1.6(5)	48(7)	2.51(1)
Eichbaumsee	−3.2(1)	74(5)	2.4(1)	26(5)	2.48(1)
Mere	−3.4(1)	63(3)	1.9(1)	37(3)	2.41(1)
Hatchmere	−3.3 (1)	70(0)	2.5(1)	30(1)	2.46(1)

[a] Chemical shifts assigned to PO_4^{3-} sequestered in Phoslock®.
[b] Chemical shifts assigned to hydroxyapatite in the sediment.
[c] Chemical shifts assigned to aluminium phosphates.

majority being applied at the deepest part of the lakes. However, the combination of vertical and horizontal translocation processes may reduce the efficiency of the LMB applications to control sediment P release at the whole lake scale, as has previously been shown for aluminium treated sediments (Lewandowski et al., 2003).

4.3. Molar La:P ratio in the sediment

The expected molar ratio of La to P in the formed La−O−P minerals is 1:1 as a lanthanum phosphate is formed, as is the case with both rhabdophane and monazite. A ratio above 1 indicates that not all La is bound to P implying either an excess P binding capacity or that the excess La present cannot bind to P. A ratio below 1 indicates that, either 1) La binds more than one phosphate ion, 2) that the P in the HCl extract (assumed to be La phosphate) is P not associated with La, or 3) that not all reactive La was extracted during the HCl extraction. The La:P ratios in six lakes exceeded this theoretical ratio after corrections for the pre-treatment background-P, (see section 2.2.1), and uncertainties associated with the measurements indicate that an additional three lakes could have ratios above one as well. However, no evidence for excess P binding capacity was observed, which indicates that the excess La in the sediment is unable to bind P.

A high DOC concentration has been reported to retard LMB P-binding processes (Lürling and Faassen, 2012; Reitzel et al., 2013; Lürling et al., 2014; Dithmer et al., this issue), and DOC concentrations in the pore waters of five of the six lakes with HCl extractable La:P > 1 (Lake Otterstedter See, Lake Rauwbraken, Lake Behlendorfer See, Hatchmere, and Lake Blankensee) were high in relation to the above studies (10 mg L^{-1}, threshold value according

to Lürling et al., 2014). Further evidence of the complication of La and DOC lies within the slightly longer La−O bond distances in the 'high DOC' lakes (Lake Rauwbraken, Lake Blankensee, Lake Behlendorfer See, and Hatchmere) compared with 'low DOC lakes', which indicates association of La with DOC within the clay (Dithmer et al., 2015a). The apparent role of DOC in confounding LMB performance in the sediments is also in agreement with the results from 16 Danish lakes, where the SRP binding capacity in the lake water was found to be negatively correlated with DOC in a seven day laboratory experiment (Dithmer et al. (this issue)), and it was found that high alkalinity may counteract the negative influence of high DOC on adsorption capacity. This could explain the high La:P ratio and low SRP adsorption capacities discussed above for Lake Otterstedter See, and to some extent for Lake Rauwbraken, which had high concentrations of pore water DOC and low surface water alkalinity. In the current study, the SRP adsorption capacity was evaluated by 24 h incubations, and the immobilization of SRP within LMB may take longer than this experimental period. Dithmer et al. (this issue) demonstrated that the apparent reduction of LMB P binding capacity in the presence of DOC can be overcome by simply increasing the incubation time; i.e. the P binding capacity is not necessarily lower, but, instead, the rate of uptake is slower.

4.4. Evidence of SRP release from the sediment

SRP sediment efflux was low for all lakes with the exception of Lake Het Groene Eiland and Lake Blankensee. The relatively high SRP efflux in Lake Het Groene Eiland was reflected by a high SRP concentration in the water column, and supported the findings by Lürling and van Oosterhout (2013a, b), who found that the restoration activities in Lake Het Groene Eiland did not result in the expected decrease in water column SRP shortly after treatment, possibly due to persistent external P loading, or an insufficient dose of LMB.

4.5. La and P binding forms identified by ^{31}P MAS NMR and La-EXAFS

Rhabdophane (LaPO$_4$·n H$_2$O) is a stable mineral, but can eventually condense thermodynamically into the even more stable monazite (LaPO$_4$) (Dithmer et al., this issue). Rhabdophane was identified as the main La phosphate mineral in nine of the ten lakes. In Lake Otterstedter See, the dominant La phosphate mineral identified by ^{31}P NMR was monazite. This finding is in agreement with Dithmer et al. (this issue) who demonstrated that aging of rhabdophane can lead to the formation of monazite. Lake Otterstedter See was the lake first treated (2006) of our ten lakes which may explain this result. Lake Silbersee was treated at the same time, but has had multiple LMB treatments subsequently, which might have influenced the ^{31}P NMR analysis as well as the EXAFS analysis, so a mixture of "older" and "newer" La phosphate minerals is apparent in the sediments of this lake. Given this explanation, one would expect a gradient of mineral formation with sediment depth.

The EXAFS showed more variation in the molecular structure of the observed La phosphate mineral than did the ^{31}P NMR analysis, with the bond-distance varying from 2.41(1) Å (Mere Mere) to 2.56 (1) Å (Lake Blankensee). The longer bond distances are most likely reflecting a mixture of rhabdophane and unreacted La in the clay matrix.

4.6. Perspective

In many lakes, legacy P is the main threat to the lake water quality. However, it is important to stress that society needs to limit

the external P loads entering our waterways before in lake measures are initiated. When this is done, the worldwide requirement for improved lake water quality calls for efficient methods and technologies for SRP removal. Several products already exist, and basic knowledge obtained from laboratory experiments can be very informative for initial dose calculations and for evaluating potential interfering substances. However, the knowledge on lake restoration products under *in situ* conditions is generally limited. The current study shows that the operational performance of LMB *in situ* is significantly different from laboratory conditions. Therefore, studies evaluating full scale effects of lake restoration products are very important for verifying/rejecting laboratory hypothesis to support wider operational considerations of lake managers. The multi lake analyses in this study has demonstrated the importance of considering the operational performance of LMB immobilizing SRP in lake bed sediments, which could aid lake managers in choosing appropriate measures to counteract lake-bed P release and to manage eutrophication across experimental scales, from laboratory controlled microcosms, to whole lake trials, and finally to multi lake analyses.

5. Conclusions

1. La was distributed across the upper 10 cm of bed sediments in most of the ten LMB-treated lakes. The majority of La was recovered in the HCl-fraction following sequential chemical extraction procedures, and rhabdophane was identified as the dominant La phosphate mineral by solid state ^{31}P NMR and EXAFS spectroscopy.
2. Excess La not bound to P in the sediment was not able to bind excess SRP during a 24 h incubation experiment, indicating that not all of the La in the LMB can bind SRP or that interactions with DOC or other chemical constituents of the receiving water acted to retard the operational performance of the material.
3. Following intact sediment core incubations, sediment SRP release was low or indicative of sediment SRP uptake, in all sampled lakes except Lake HG Eiland and Lake Blankensee where significant release was reported at the time of sampling.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.02.011.

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