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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 2006-2013 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

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29 the LMB towards the deepest areas of the lakes. Lanthanum was generally recovered from bed

30 sediment samples following sequential chemical extraction from the HCl fraction. Soluble reactive

31 P (SRP) release experiments on intact sediment cores indicated conditions of P retention (with the

32 exception of two lakes) by sediments, indicating effective control of sediment P release, i.e.

33 between two and nine years after treatment.

1   Introduction

35 Eutrophication of freshwaters is a global problem caused mainly by elevated phosphorus (P)

36 concentrations in the sediment due to P emissions from agriculture and sewage. Control and

37 regulation of these emissions have improved significantly in recent years, in order to fulfil

38 legislation on water quality, such as the European Water Framework Directive (European Union

39 2000). However, the release of legacy stores of P in lake bed sediments can confound catchment

40 management by maintaining elevated water column TP concentrations for decades and may also

41 need to be controlled. Chemical lake restoration, also referred to as geo-engineering, has been

42 demonstrated as a measure for controlling sediment P release resulting in rapid chemical recovery

43 following catchment management (Mackay et al., 2014; Spears et al., 2014). To date, chemicals

44 including iron (Fe) and aluminium (Al) in the form of oxides and hydroxides have been widely used

45 for P control in lakes (Boers et al., 1992; Cooke et al., 1993; Welch and Schrieve, 1994; Welch and

46 Cooke, 1999; Lewandowski et al., 2003; Reitzel et al. 2005a) but engineered materials like the

47 lanthanum-modified bentonite Phoslock® (LMB) (Douglas et al. 1999, 2002; Copetti et al., this

48 issue) have received increasing attention in recent years. Most published literature on LMB has

49 focused on laboratory or mesocosm studies (Egemose et al.,2010; Reitzel et al., 2012; Reitzel et al.,

50 2013; Bishop et al., 2014; Lürling et al., 2014), with assessment of chemical and ecological

51 responses of LMB treated lakes being relatively rare (van Oosterhout and Lürling, 2011; Meis et al.,

52 2012; Crosa et al., 2013; Spears et al., this issue). Spears et al. (2013a and this issue) demonstrated

2

53 the importance of considering field scale responses following applications across multiple treated

54 lakes, providing evidence to support laboratory based trials.

55 In general, laboratory studies on LMB have included studies concerning either toxicity or P binding

56 efficiency of LMB (Copetti et al., this issue). Toxicity studies have shown that La accumulates in

57 organisms (e.g. crayfish) but without noticeable side-effects (van Oosterhout et al., 2014), and does

58 not appear to limit the growth of aquatic macrophytes in the field (Gunn et al., 2014; Spears et al.,

59 this issue; Copetti et al., this issue). Studies on the efficiency of LMB performed under different

60 environmental conditions have shown that at pH above 8.5 interference with the binding of soluble

61 reactive phosphorus (SRP) to LMB can occur (Ross et al., 2008; Vopel et al., 2008; Egemose et al.,

62 2010; Gibbs et al., 2011; Reitzel et al., 2013). Moreover, under low alkalinity conditions dispersion

63 of the clay matrix can result in higher concentrations of La in the lake water (Spears et al., 2013a),

64 but also an improved SRP binding capacity (Reitzel et al., 2013). Elevated concentrations of

65 dissolved organic carbon (DOC) in the water column appear to reduce the SRP binding

66 performance of LMB over short time scales by reducing the formation of the La phosphate, as

67 demonstrated by Lürling et al. (2014) and Dithmer et al (this issue). However, a negative impact of

68 DOC on binding performance appears to be overcome with time (Dithmer et al., this issue). In

69 general, these observations suggest lower than expected P control by LMB in full scale treatments,

70 when compared to theoretical binding capacity used to estimate product dose (i.e. 1 tonne LMB to

71 control 11 kg P).

72 Knowledge on the performance of LMB in bed sediments under natural conditions is limited (Meis

73 et al., 2012, 2013). We address this knowledge gap by examining the behaviour of LMB and its

74 interactions with phosphate and other substances present in the bed sediments across 10 treated

75 lakes (Table 1). Specific La phosphate mineral formation is assessed (using extended x-ray

76 absorption fine spectroscopy (L$_{III}$ EXAFS) and solid state ^{31}P MAS NMR) within bed sediments of

77 treated lakes to determine that La and P had precipitated as Rhabdophane ($LaPO_4 \cdot nH_2O$). Sediment

78 profiles of both La and P were constructed to determine vertical sediment mixing of La following

79 LMB applications, to test the hypothesis that LMB will be vertically and horizontally mobile in bed

80 sediments following application. Finally, to determine the operational performance of the LMB

81 treatments, we quantified SRP efflux from intact sediment cores, the P binding capacity of bed

82 sediments, and La and P composition across operationally defined sediment P pools using a

83 standard sequential chemical extraction procedure. The implications of these results for the wider

84 application of LMB are discussed.

85 ## 2   Methods and materials

86 ### 2.1   Study sites and sample collection

87 Ten lakes; United Kingdom (UK) (2), Germany (DE) (5), and the Netherlands (NL) (3)), treated

88 between November 2006 and March 2013 with LMB, were sampled in June 2014. The treatments

89 were performed with LMB applied as slurry from a boat or barge to all lakes; however small

90 variations in the treatment procedures including the use of low doses of flocculants were conducted

91 in some cases (Table 1).

92 Sediment cores were collected from a boat at the deepest part of each lake (12 cores for each UK

93 lake and 11 cores for each of the Dutch and German lakes) with a Kajak gravity corer (Ø = 5.2 cm),

94 with the exception of Lake Blankensee, where the sampling was conducted at a fixed sampling spot

95 with a depth of 1.5 m. Epilimnetic lake waters were sampled, and following filtration (cellulose

96 acetate membrane filter 0.45 µm), alkalinity (Gran Plot titration), dissolved organic carbon (DOC;

97 infrared spectrophotometric analysis using a Shimadzu TOC 5000 Total organic carbon analyser)

98 and SRP concentrations (spectrophotometric analysis; Koroleff 1983) were determined. In Figure 1,

99 the various analyses performed on the sediment are shown.

100   On collection, three sediment cores were sectioned for sequential P and La extraction. The upper 10

101   cm of the sediment cores were sliced in one cm intervals and identical sediment depth layers from

102   each of the three cores were pooled into one composite sample. An exception was made for Lake

103   Otterstedter See and Lake Blankensee, where the upper 6 cm and 3 cm were pooled, respectively,

104   and the following 10 cm were sliced in 1 cm thicknesses, upon request from the lake managers.

105   Four additional cores were sectioned as above and samples were pooled in zipper storage bags for

106   SRP sorption experiments, pore water analysis of DOC and ^{31}P MAS NMR and La L_{III} EXAFS

107   spectroscopy. Furthermore, four (NL, DE) or five (UK) intact sediment cores were brought back to

108   the lab and used for the SRP flux experiment (section 2.2.2.).

109   From the pooled sediment samples, approximately 5 g sub-samples were removed, dried at ambient

110   temperature and used for the determination of total La (TLa) and total P (TP) concentrations using

111   Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Optima 2100 DV, Perkin

112   Elmer (standard deviation on replicate samples of less than 2 %). Following this analysis, the

113   sediment depth sample with the highest TLa concentration was used for ^{31}P MAS NMR and L_{III}

114   EXAFS analyses. Dry weight (DW) was determined by drying sediment at 105°C for 24 hours and

115   loss on ignition (LOI) by combusting subsamples of the dried sediment for 5h at 520°C.

116   **2.2   Sediment analysis**

117   **2.2.1   Vertical distribution of La and P pools in the sediment**

118   Fresh sediment (1.0 g) from each pooled sediment sample was sacrificed for the determination of

119   operationally defined sediment P pools using a modified chemical extraction procedure (Reitzel,

120   2005b). The TLa and TP concentrations recovered following sequential extractions in water (H_2O),

121   bicarbonate dithionite ($HCO_3^-/S_2O_4^{2-}$; BD), sodium hydroxide (NaOH), hydrochloric acid (HCl)

122   and residual (Res) were determined using ICP-OES. Total La and TP analyses were performed on

123   subsamples of the pooled sediment following addition of concentrated nitric acid (HNO_3) and

124 combustion in a microwave oven for 15 minutes prior to analysis by ICP-OES. Sediment densities

125 in the respective layers were calculated and used to express the amount of La and P per unit surface

126 area of sediment (expressed as mmol m^{-2}).

127 Generally, the HCl treatment is known to extract calcium phosphates from sediments (e.g. Reitzel

128 2005b). In addition, previous studies have shown that most of the La bound P is recovered in the

129 HCl extract (Meis et al., 2011; Reitzel et al., 2013a). Hence, the La:P binding ratio in the HCl

130 extracts can be used to evaluate whether all the La sites of the LMB are binding P. Given the lack of

131 pre-application data available from the studied lakes on sediment P properties it was assumed that

132 the HCl-P concentrations in the LMB treated sediment at depths where the HCl-La concentration

133 approached zero represented background HCl-P conditions, further assuming a uniform background

134 concentration of HCl-P throughout the sediment profile, as seen in e.g. Jensen & Thamdrup 1993

135 and Reitzel et al. 2005a. The total amount of La phosphate as a result of the LMB treatment was

136 estimated by subtracting the background HCl-P amounts from the amount of HCl-P in the sediment

137 layers containing La. This procedure was used for Lake Rauwbraken, Lake Blankensee, Lake Het

138 Groene Eiland, Lake Behlendorfer See, Lake Eichbaumsee and Hatchmere. For the remaining lakes

139 the HCl fraction of all layers contained La. Consequently, it was assumed that all the HCl-P solely

140 reflected La phosphate, which most likely overestimates the La phosphate content in sediment

141 layers of these lakes.

142 **2.2.2 SRP flux experiments on intact sediment cores**

143 The SRP flux across the sediment-water interface was measured at room temperature (20 °C) in

144 either four (NL, DE) or five (UK) replicate intact sediment cores incubated for 22-30 hours under

145 oxic conditions (i.e. no lid on the cores), corresponding to the natural conditions in the lake, at the

146 time of sampling. Samples for SRP concentrations were collected from the water overlying the

147 sediment in each core at the beginning and at the end of the incubation periods. The SRP

148 concentrations were related to water volume and surface area in the sediment cores to express SRP

149 flux per unit area per day (mmol m^{-2} d^{-1}).

150 **2.2.3 SRP adsorption experiments**

151 The SRP binding capacity of each sediment layer was determined by suspending 1 g fresh sediment

152 (n=3) from each layer of the pooled sediment (from four cores, see section 2.1) in 40 mL purified

153 water containing 1.98 mg L^{-1} SRP added as K_2HPO_4, with pH adjusted to 6.5 using NaOH. Soluble

154 reactive P concentrations were measured before and after incubation for approx. 24 h on a shaking

155 table, followed by separation of sediment and solution by centrifugation (10 min, RCF=1200),

156 filtration of the supernatant (cellulose acetate membrane filter 0.45 µm) and acidification of the

157 filtrate (2 M sulphuric acid).

158 **2.2.4 Pore water analysis**

159 Pore water DOC concentrations were determined following collection of 4 mL of pore water from

160 each of the composite sediment samples after centrifugation (10 min, RCF 1200) and filtration

161 (cellulose acetate membrane filter0.45 µm).

162 **2.2.5 Solid state ^{31}P MAS NMR**

163 Solid state ^{31}P MAS NMR spectra were obtained for the sediment layer containing the highest La

164 concentrations from each lake. The measurements were conducted on a Varian INOVA 500 MHz

165 instrument with a spinning speed of 10 kHz, 8 s relaxation time and 5000 or 10000 scans depending

166 on the TP concentration. The ^{31}P MAS NMR spectra were deconvoluted using SpinWorks 3.1.8.1

167 (Marat, 2011).

168 **2.2.6 L$_{III}$-EXAFS**

169 To study La phases in the sediment EXAFS measurements were performed at beamline I811,

170 MAX-lab, Lund University, Sweden, which operated at 1.5 GeV and a current of 250 mA. The X-

171 ray beam was detuned to minimize higher-order harmonics, and data were obtained in fluorescence

172 mode with a PIPS detector. Five consecutive scans of 180 s were measured at the La L$_{III}$-edge

173 (5483eV) of finely ground sediment samples from the layer containing the highest La concentration

174 from each lake.

175 In all spectra, double electron excitations were observed, an anomalous feature common in EXAFS

176 for lanthanides (Solera et al. 1995, Ohta et al. 2008). This was removed with built-in functions in

177 EXAFSPAK (George, 2000). In addition, the Barium (Ba) L$_{II}$-edge (at 5624 eV) was observed. This

178 interference is caused by the Ba content in the LMB (620 µg Ba g^{-1} DW (Spears et al., 2013b)),

179 naturally occurring Ba in the bed sediments (e.g. 5-600 µg Ba g^{-1} DW in Clatto Reservoir, UK

180 (Meis et al., 2012)) or both. A pre-treatment sediment sample from Loch Flemington, UK, was used

181 as reference to counteract for this interference, by performing a baseline subtraction of a linearly

182 scaled background measurement with a strong Ba L$_{II}$ peak, effectively removing the interfering Ba

183 peak without affecting the rest of the data set. Data treatment was performed in EXAFSPAK and

184 afterwards fitted with scattering paths obtained with FEFF 7.02 (Zabinsky et al., 1995). The data

185 were analyzed using refinement of single-scattering La-O distances, and the distances for pure

186 synthesized rhabdophane (LaPO$_4$ · H$_2$O) is 2.47(1) Å and for monazite (LaPO$_4$) 2.52(1) Å (Dithmer

187 et al., 2015) were used as initial distances. Additional scattering pathways (La--P, La-O-P, La--C,

188 La-O-C) were included with fixed average distances determined from ICDD and FEFF-calculations,

189 and not refined due to the complexity of the EXAFS data.

190 ## 2.3 Statistical analyses

191 Pearson's correlations were performed to allow examination of responses and potential drivers

192 operating across the studied lakes. Only relevant significant ($p < 0.05$) correlations are reported.

193 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 (Figure 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 (Figure 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 (4.5w/w % La in the LMB) (Table 2). The applied La dose varied between 71-228 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 - 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 (Figure 4) and there were no significant positive correlations between

9

216 the SRP adsorption capacities and TLa, with the exception of Lake Otterstedter See (Pearson´s r =

217 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

219 The sediment SRP efflux was close to zero for eight of the lakes (Hatchmere, Mere Mere, Lake

220 Rauwbraken, Lake Kuil, Lake Silbersee, Lake Behlendorfer See, Lake Otterstedter See, and Lake

221 Eichbaumsee; range of -1.6±6.0 to 0.3±5.1 mg SRP $m^{-2}d^{-1}$) (Table 4). Lake Het Groene Eiland

222 (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

223 from the sediments to the water column.

3.4 Pore water analysis

225 Pore water DOC concentrations in Lake Het Groene Eiland were below 6 mg DOC L^{-1} for all

226 sediment layers, whereas concentrations in Lake Otterstedter See, Hatchmere, and Lake

227 Rauwbraken were all above 15 mg L^{-1}, with the remaining six lakes ranging between 5-15 mg L^{-1}

228 (Figure 4).

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

3.5.1 ^{31}P MAS NMR spectroscopy

231 The sediment depth layer with the highest La concentration from each lake was analysed by ^{31}P

232 NMR to determine the P forms in the treated sediment. Rhabdophane (LaPO$_4$ · n H$_2$O) was

233 identified in all samples and characterized by an isotropic chemical shift, δ_{iso}, of -3.1(1) to -3.9(5)

234 ppm, with the exception of Lake Otterstedter See (δ_{iso} = -4.5(1) ppm) which was assigned to

235 monazite (LaPO$_4$; Table 5; Figure SI-1). The chemical shifts assigned to rhabdophane varied

236 slightly compared to rhabdophane in pure LMB samples (Dithmer et al., 2015), which is explained

237 by interference from external factors such as e.g. Fe in the sediment causing a small downfield shift.

10

238   The second relevant P-species identified was assigned to hydroxyapatite ($Ca_{10}(PO_4)_3(OH)$), with a

239   chemical shift at 1.5(5)-2.5(3) ppm (Shand et al. 1999, Cade-Menun 2005, Dougherty et al. 2005)

240   and constituted 20-60% of the total intensity (Table 5). Phosphate species adsorbed to the surface of

241   rhabdophane were expected (Dithmer et al, 2015), but the position of this resonance (δ_{iso} = -0.48

242   ppm, Dithmer et al. 2015) is between that of hydroxyapatite and bulk rhabdophane. Thus, it is

243   masked by the broadness of the spectra.

244   **3.5.2   La L_{III}-EXAFS**

245   The sediment samples from the ^{31}P NMR study were also analysed by EXAFS (Table 5). The bond-

246   distances, d_{La-O}, were determined from extracted k^3-weighted $X(k)$ functions and the corresponding

247   Fourier Transforms (Figure SI-2). The distances were assigned to be representative for

248   rhabdophane, except in Lake Behlendorfer See (2.51(1) Å) and Lake Blankensee 2.56(1) Å), which

249   were assigned to either monazite or a mixture of rhabdophane, monazite and unreacted La in the

250   clay matrix, as previously observed by Dithmer et al. (2015). The La concentrations in sediment

251   samples from Lakes Silbersee and Het Groene Eiland were too low for a reliable analysis of the

252   EXAFS data.

253   **4   Discussion**

254   This study demonstrated that LMB treatment of the ten lakes resulted in the sequestration of P in

255   the form of rhabdophane. In addition, LMB was generally mixed vertically in the sediments at the

256   deepest area of the lakes, which may have resulted in reduced P removal efficiency at the sediment

257   water interface at the whole lake scale, depending on the depth of the sediment layer that interacts

258   with the water body. However, at the sampling stations, the lakes generally had a low SRP sediment

259   efflux at the time of sampling indicating that LMB, or other P binding properties of the bed

260   sediments, controlled the release of P across the sediment-water interface. The La:P ratios in the

261   sediments were generally above 1, which indicates that not all La had reacted with P yet. However,

262   these La containing layers did not display any increased SRP binding capacity. These two

263   observations indicate there is no unreacted La available for additional sequestration of P.

264   **4.1   Speciation of La and P in the sediment**

265   The sequential La and P extractions showed that the majority of TLa and TP were recovered

266   following HCl extraction, in agreement with earlier findings by Meis et al. (2011) and Reitzel et al.

267   (2013), and in agreement with the fact that HCl is generally known to dissolve mineral phases. This

268   is further supported by the ^{31}P NMR EXAFS results which demonstrated that the main La

269   phosphate formed was rhabdophane. The only exception was Lake Otterstedter See where 45 % of

270   the La was recovered following NaOH extraction and 39 % of the La was recovered following HCl

271   fraction. This may be due to complexation of La and organic matter extracted by the NaOH solution

272   (e.g. Reitzel et al., 2005).

273   Residual-La constituted up to 60 % of the HCl-La fraction in a Danish eutrophic lake sediment

274   manipulated under laboratory-controlled conditions (Reitzel et al. 2012). However, a significant

275   positive correlation was observed between the HCl-La and Res-La concentrations. A possible

276   explanation for this is that the HCl extraction does not extract all La in the samples during the

277   extraction time used (1 hour followed by a 5 min extraction). Hence, the second extraction time

278   may be too short to extract all La. Alternatively, carbonates present in the clay matrix may lower

279   the extraction efficiency of the HCl solution. This agrees well with the observation that the highest

280   Res-La content was observed for the three lakes with highest alkalinity (Lake Het Groene Eiland,

281   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 bioturbation by animals such as chironomids (as shown by Reitzel et al. 2012), sediment mixing behavior 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 et al., 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 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

13

306   to control sediment P release at the whole lake scale, as has previously been shown for aluminum

307   treated sediments (Lewandowski et al., 2003).

308   ## 4.3   Molar La:P ratio in the sediment
309

310   The expected molar ratio of La to P in the formed La-O-P minerals is 1:1 as a lanthanum phosphate

311   is formed, as is the case with both rhabdophane and monazite. A ratio above 1 indicates that not all

312   La is bound to P implying either an excess P binding capacity or that the excess La present cannot

313   bind to P. A ratio below 1 indicates that, either 1) La binds more than one phosphate ion, 2) that the

314   P in the HCl extract (assumed to be La phosphate) is P not associated with La, or 3) that not all

315   reactive La was extracted during the HCl extraction. The La:P ratios in six lakes exceeded this

316   theoretical ratio after corrections for the pre-treatment background-P, (see section 2.2.1), and

317   uncertainties associated with the measurements indicate that an additional three lakes could have

318   ratios above one as well. However, no evidence for excess P binding capacity was observed, which

319   indicates that the excess La in the sediment is unable to bind P.

320   A high DOC concentration has been reported to retard LMB P-binding processes (Lürling and

321   Faassen, 2012; Reitzel et al., 2013; Lürling et al., 2014; Dithmer et al. this issue), and DOC

322   concentrations in the pore waters of five of the six lakes with HCl extractable La:P > 1 (Lake

323   Otterstedter See, Lake Rauwbraken, Lake Behlendorfer See, Hatchmere, and Lake Blankensee)

324   were high in relation to the above studies (10 mg L^{-1}, threshold value according to Lürling et al.,

325   2014). Further evidence of the complication of La and DOC lies within the slightly longer La-O

326   bond distances in the 'high DOC' lakes (Lake Rauwbraken, Lake Blankensee, Lake Behlendorfer

327   See, and Hatchmere) compared with 'low DOC lakes', which indicates association of La with DOC

328   within the clay (Dithmer et al., 2015). The apparent role of DOC in confounding LMB performance

329   in the sediments is also in agreement with the results from 16 Danish lakes, where the SRP binding

330   capacity in the lake water was found to be negatively correlated with DOC in a seven day

14

331 laboratory experiment (Dithmer et al. (this issue)), and it was found that high alkalinity may

332 counteract the negative influence of high DOC on adsorption capacity. This could explain the high

333 La:P ratio and low SRP adsorption capacities discussed above for Lake Otterstedter See, and to

334 some extent for Lake Rauwbraken, which had high concentrations of pore water DOC and low

335 surface water alkalinity. In the current study, the SRP adsorption capacity was evaluated by 24 h

336 incubations, and the immobilization of SRP within LMB may take longer than this experimental

337 period. Dithmer et al. (this issue) demonstrated that the apparent reduction of LMB P binding

338 capacity in the presence of DOC can be overcome by simply increasing the incubation time; i.e. the

339 P binding capacity is not necessarily lower, but, instead, the rate of uptake is slower.

340 **4.4   Evidence of SRP release from the sediment**
341

342 SRP sediment efflux was low for all lakes with the exception of Lake Het Groene Eiland and Lake

343 Blankensee. The relatively high SRP efflux in Lake Het Groene Eiland was reflected by a high SRP

344 concentration in the water column, and supported the findings by Lürling and van Oosterhout

345 (2013), who found that the restoration activities in Lake Het Groene Eiland did not result in the

346 expected decrease in water column SRP shortly after treatment, possibly due to persistent external P

347 loading, or an insufficient dose of LMB.

348 **4.5   La and P binding forms identified by ^{31}P MAS NMR and La-EXAFS**

349 Rhabdophane (LaPO$_4 \cdot n$ H$_2$O) is a stable mineral, but can eventually condense thermodynamically

350 into the even more stable monazite (LaPO$_4$) (Dithmer et al. this issue). Rhabdophane was identified

351 as the main La phosphate mineral in nine of the ten lakes. In Lake Otterstedter See, the dominant La

352 phosphate mineral identified by ^{31}P NMR was monazite. This finding is in agreement with Dithmer

353 et al. (this issue) who demonstrated that aging of rhabdophane can lead to the formation of

354 monazite. Lake Otterstedter See was the lake first treated (2006) of our ten lakes which may explain

355   this result. Lake Silbersee was treated at the same time, but has had multiple LMB treatments

356   subsequently, which might have influenced the ^{31}P NMR analysis as well as the EXAFS analysis,

357   so a mixture of "older" and "newer" La phosphate minerals is apparent in the sediments of this lake.

358   Given this explanation, one would expect a gradient of mineral formation with sediment depth.

359   The EXAFS showed more variation in the molecular structure of the observed La phosphate

360   mineral than did the ^{31}P NMR analysis, with the bond-distance varying from 2.41(1) Å (Mere Mere)

361   to 2.56 (1) Å (Lake Blankensee). The longer bond distances are most likely reflecting a mixture of

362   rhabdophane and unreacted La in the clay matrix.

363

364   **4.6   Perspective**

365   In many lakes, legacy P is the main threat to the lake water quality. However, it is important to

366   stress that society needs to limit the external P loads entering our waterways before in lake

367   measures are initiated. When this is done, the worldwide requirement for improved lake water

368   quality calls for efficient methods and technologies for SRP removal. Several products already

369   exist, and basic knowledge obtained from laboratory experiments can be very informative for initial

370   dose calculations and for evaluating potential interfering substances. However, the knowledge on

371   lake restoration products under *in situ* conditions is generally limited. The current study shows that

372   the operational performance of LMB *in situ* is significantly different from laboratory conditions.

373   Therefore, studies evaluating full scale effects of lake restoration products are very important for

374   verifying/rejecting laboratory hypothesis to support wider operational considerations of lake

375   managers. The multi lake analyses in this study has demonstrated the importance of considering the

376   operational performance of LMB immobilizing SRP in lake bed sediments, which could aid lake

377   managers in choosing appropriate measures to counteract lake-bed P release and to manage

378   eutrophication across experimental scales, from laboratory controlled microcosms, to whole lake

379   trials, and finally to multi lake analyses.

380   **5   Conclusions**

381   1. La was distributed across the upper 10 cm of bed sediments in most of the ten LMB-treated

382   lakes. The majority of La was recovered in the HCl-fraction following sequential chemical

383   extraction procedures, and rhabdophane was identified as the dominant La phosphate

384   mineral by solid state ^{31}P NMR and EXAFS spectroscopy.

385   2. Excess La not bound to P in the sediment was not able to bind excess SRP during a 24 hour

386   incubation experiment, indicating that not all of the La in the LMB can bind SRP or that

387   interactions with DOC or other chemical constituents of the receiving water acted to retard

388   the operational performance of the material.

389   3. Following intact sediment core incubations, sediment SRP release was low or indicative of

390   sediment SRP uptake, in all sampled lakes except Lake HG Eiland and Lake Blankensee

391   where significant release was reported at the time of sampling.

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Figure 1. Overview of the analysis performed on the sediment cores from the ten lakes**.**

Figure 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.

Figure 3: The HCl-extractable content of La (white) and P (black) in the sediment profile of the ten LMB treated lakes.

Figure 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).

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[a]	4.5	5.0	0.8	9.6	59[1]	35(2)[11]	n/a	n/a
Silbersee[b]	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) [c, e]	2.6	8.8	0.4	4.7	133(143)[3]	15 (13)1[12]	28 (85)[3]	4 (6)[12]
H. G. Eiland[b]	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[b]	DE	nov-10	Flocculent (PAC)[e]	23.2	6.5	2.5	5.9	358[8]	91[15]	32[8]	28[18]
Mere Mere	UK	mar-13		15.8	2.8	1.3	14.4	77[16]	75[17]	16[16]	13[17]
Hatchmere	UK	mar-13		4.7	1.4	2.0	16.7	83[16]	73[17]	18[16]	32[17]

[a]Nowak (2006), [b]Nowak (2008), [c]Lürling and van Oosterhout (2013) , [d]Lürling and van Oosterhout (2012), [e]PAC (polyaluminumchloride), [f]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.

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)

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

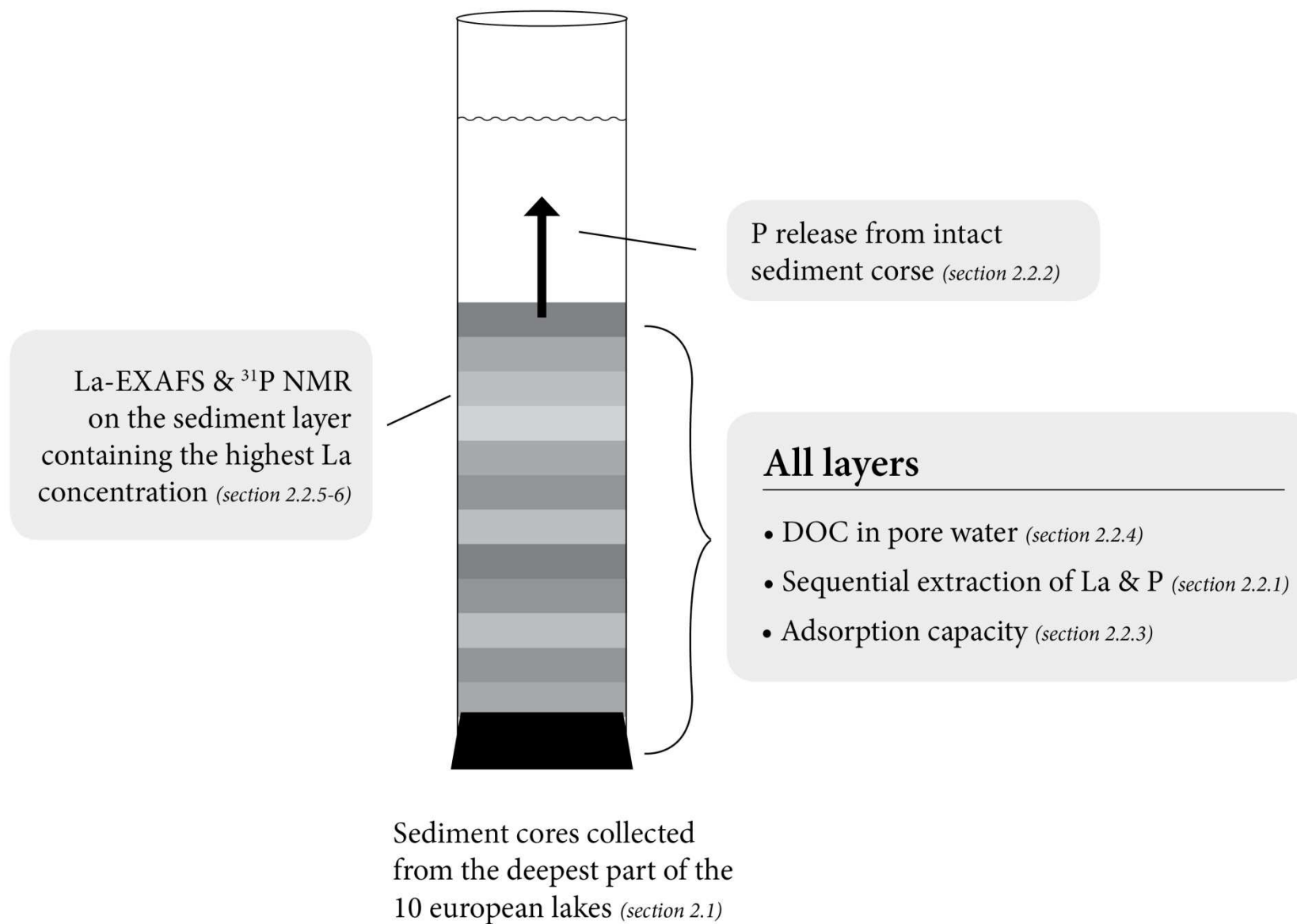|	Res-La	T La	HCl-P
HCl-La	Otterstedter(0.84) Silbersee (0.96) Rauwbraken (0.99) HG Eiland (0.93) Kuil (0.97) Behlendorfer (0.76) Eichbaum (0.93) Mere (0.89) Hatchmere (0.98)	Rauwbraken (1.0) Kuil (0.65) Blankensee (0.81) Behlendorfer (0.95) Eichbaum (0.96) Hatchmere (0.96)	Silbersee (0.79) Rauwbraken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

Table 4: SRP release and standard deviations from intact sediment cores collected in the ten LMB treated lakes
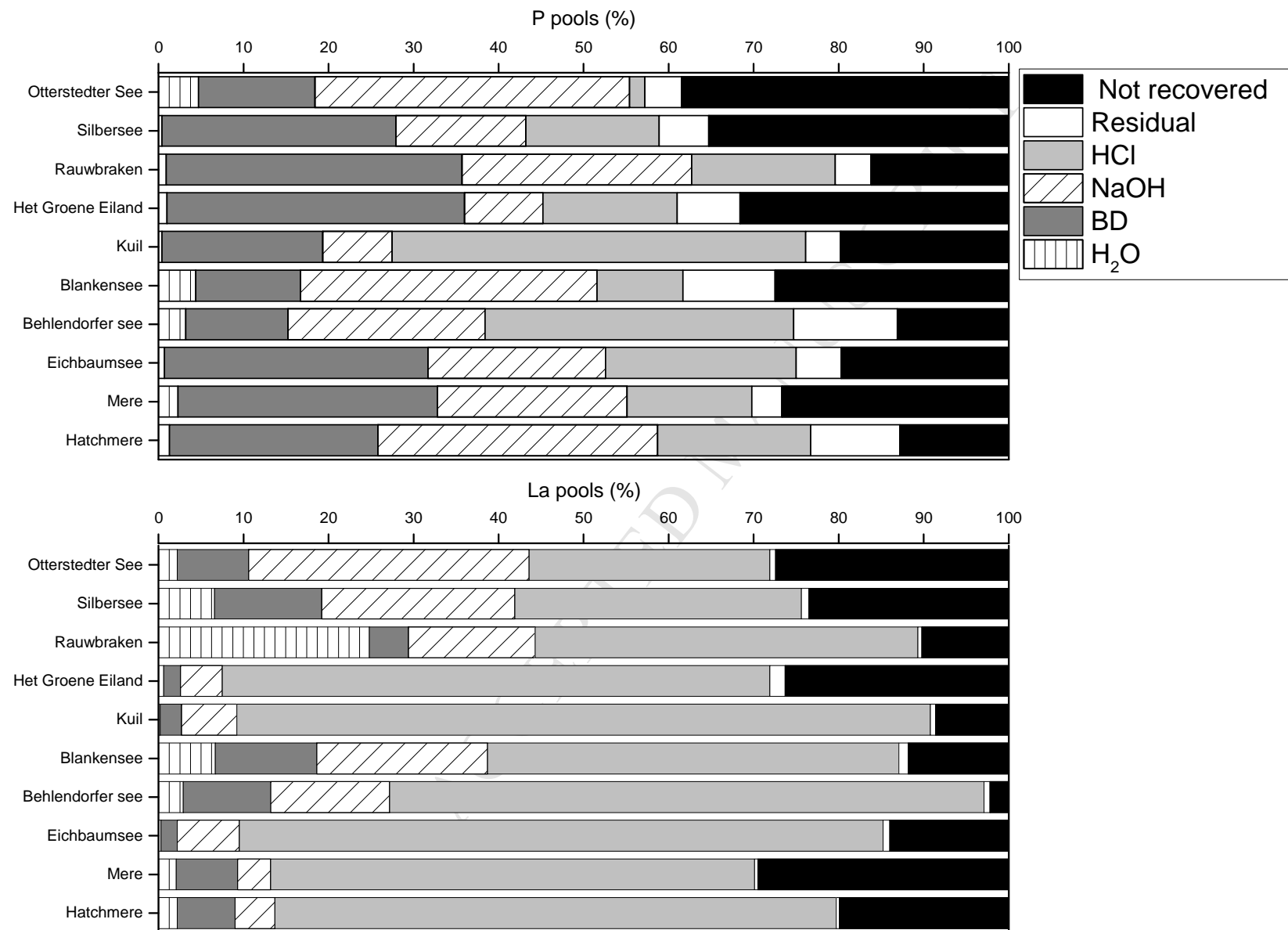
Lake	SRP Release (mg P·m⁻²·d⁻¹)
Otterstedter	0.2 ± 4.1
Silbersee	0.1 ± 2.8
Rauwbraken	-0.7 ± 4.7
H. G. Eiland	10.8 ± 11.5
Kuil	0.3 ± 5.1
Blankensee	9.2 ± 4.6
Behlendorfer	1.1 ± 13.8
Eichbaumsee	-1.6 ± 6.0
Mere Mere	0.0 ± 1.4
Hatchmere	-0.2 ± 0.4

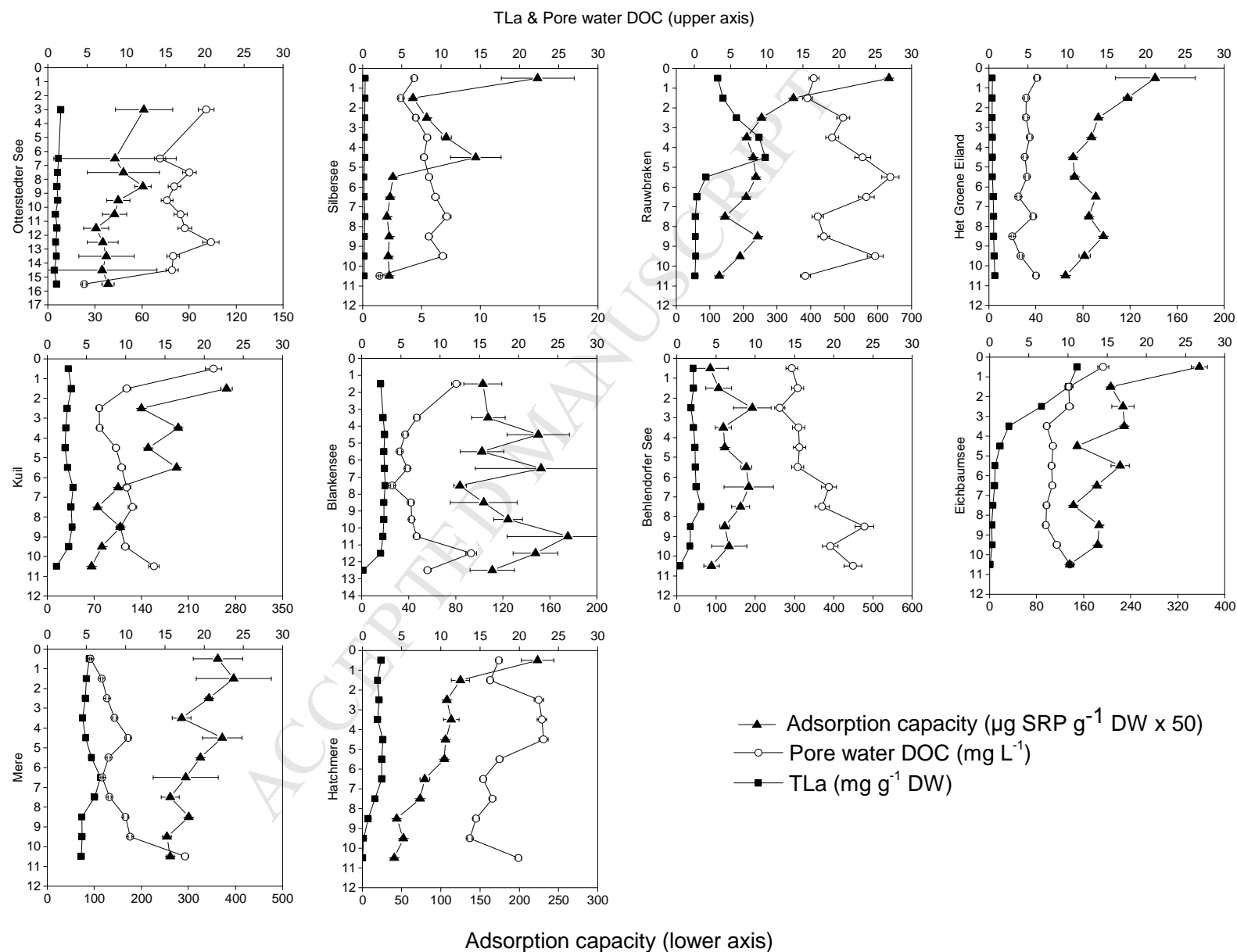**Table 5**: The results from the ^{31}P NMR and EXAFS analyses. Standard deviations shown in brackets.

Lake	^{31}P NMR				EXAFS
	δ_{iso} (ppm)[a]	I (%)[a]	δ_{iso}(ppm)[b]	I(%)[b]	$d_{La\text{-}O}$ (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.

P release from intact sediment corse *(section 2.2.2)*

La-EXAFS & ^{31}P NMR on the sediment layer containing the highest La concentration *(section 2.2.5-6)*

All layers

- DOC in pore water *(section 2.2.4)*
- Sequential extraction of La & P *(section 2.2.1)*
- Adsorption capacity *(section 2.2.3)*

Sediment cores collected from the deepest part of the 10 european lakes *(section 2.1)*

P pools (%)

La pools (%)

TLa & Pore water DOC (upper axis)

Adsorption capacity (lower axis)

Highlights

- Soluble reactive P (SRP) was sequestered as rhabdophane in ten lanthanum modified bentonite (LMB) treated European lakes.

- SRP efflux from sediment in sediment cores was suppressed in 8 out of ten lakes at time of sampling.

- LMB was focused to the deepest areas of the lakes, and mixed more than ten cm into the sediment.

- Not all added La was involved in SRP binding.

- Confounding factors such as DOC could be responsible for the lower than expected La phosphate formation.