



Evaluation of dried amorphous ferric hydroxide CFH-12® as agent for binding bioavailable phosphorus in lake sediments

Elisabeth Fuchs^{a,1}, Ana Funes^{b,c,1}, Katrin Saar^d, Kasper Reitzel^a, Henning S. Jensen^{a,*}

^a Institute of Biology, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark

^b Departamento de Ecología, Facultad de Ciencias, Universidad de Granada, 18071, Spain

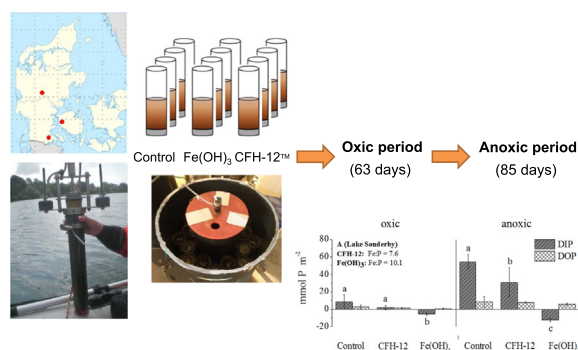
^c Instituto Del Agua, Universidad de Granada, 18071, Spain

^d Centre for Limnology, Estonian University of Life Sciences, Estonia

HIGHLIGHTS

- Redox insensitive lake restoration tool suitable for hard and soft water lakes
- Core incubation (oxic and anoxic conditions) and ageing experiments with CFH-12
- Study of sediment cores treated with CFH-12 and Fe(OH)₃ of three Danish lakes
- Reduction of P efflux in all lakes, while Fe²⁺ efflux remains unchanged by CFH-12
- No ageing effect in lake water of CFH-12 compared to freshly prepared Fe(OH)₃

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 December 2017

Received in revised form 1 February 2018

Accepted 6 February 2018

Available online 20 February 2018

Editor: Jay Gan

Keywords:

Lake restoration
P sorbent
Iron oxyhydroxide
Iron reduction
Internal P loading

ABSTRACT

Metal hydroxides formed from aluminum (Al) and iron (Fe) salts can be used as phosphorus (P) adsorbents in lake restoration, but the application entails problems in low-alkaline lakes due to acid producing hydrolysis and potential formation of toxic metal ions. Therefore, we tested the potential of applying CFH-12® (Kemira) – a dried, amorphous Fe-oxide with no pH effect – in lake restoration. Since Fe³⁺ may become reduced in lake sediments and release both Fe²⁺ and any associated P we also evaluated the redox sensitivity of CFH-12® in comparison with freshly formed Fe(OH)₃. CFH-12® was added to undisturbed sediment cores from three Danish lakes relative to the size of their mobile P pool (molar Fe:P_{Mobile} dose ratio of ~10:1), and P and Fe fluxes across the sediment-water interface were compared with those from untreated cores and cores treated with freshly formed Fe(OH)₃. Under anoxic conditions, we found that CFH-12® significantly reduced the P efflux from the sediments (by 43% in Lake Sønderby, 70% in Lake Hampen and 60% in Lake Hostrup) while the Fe²⁺ efflux remained unchanged relative to the untreated cores. Cores treated with freshly formed Fe(OH)₃ retained more P, but released significantly more Fe²⁺, indicating continued Fe³⁺ reduction. Finally, experiments with pure phases showed that CFH-12® adsorbed less P than freshly formed Fe(OH)₃ in the short term, but was capable of adsorbing up to 70% of P adsorbed by Fe(OH)₃ over 3 months. With product costs only 30% higher than Al salts we find that CFH-12® has potential for use in restoration of low-alkaline lakes.

© 2018 Elsevier B.V. All rights reserved.

* Corresponding author.

E-mail address: hsj@biology.sdu.dk (H.S. Jensen).

¹ These authors contributed equally to the publication.

1. Introduction

Phosphorus (P) is the major limiting nutrient in freshwaters (e.g. Correll, 1998) and thus, lowering of lake water P concentrations is the main target in lake restoration efforts (Schindler et al., 2016). External P sources must be reduced prior to any restoration attempts, but even then, improvement of lake water quality is often delayed due to P release from the sediment, the so-called internal P loading (Søndergaard et al., 2003). Geoengineering by adding P binding agents is thus far one of the best options for restoration purposes to reduce high lake water P caused by internal P loading in smaller lakes (Spears et al., 2013a). So far, aluminum (Al) salts forming P binding $\text{Al}(\text{OH})_3$ in reaction with water at neutral pH are the most frequently used products (Huser et al., 2015), however, the acid producing hydrolysis of most Al salts poses the risk of toxic Al^{3+} formation in low-alkaline lakes (Gensemer and Playle, 1999). One alternative is the addition of iron (Fe) salts resulting in the formation of P binding (ferric) Fe hydroxides (Jensen et al., 1992; Kleeberg et al., 2013; Rothe et al., 2014), although also the hydrolysis of Fe salts causes a decrease in pH and can release potentially toxic ions (Bakker et al., 2016). Moreover, Fe is rather redox sensitive and often loses its P binding properties in anoxic sediment over time (Kleeberg et al., 2013), especially if reduced iron (Fe^{2+}) is precipitated with sulfide in the sediment (e.g. Hupfer and Lewandowski, 2008). So far, the general assumption has been that the use of Fe for permanent P fixation requires continuous aeration of the sediment surface (Jaeger, 1994). Recent studies indicate, however, that both continuous and single Fe additions may have long-lasting effects on P burial in sediments (Bakker et al., 2016; Rothe et al., 2014). The uncertainties regarding the use of Al and Fe salts in some types of lakes have sparked a growing interest in testing and developing new materials for efficient binding of P such as magnetic Fe particles (de Vicente et al., 2010; Funes et al., 2016), zirconium oxide nano particles (Su et al., 2013) and lanthanum-modified bentonite (Copetti et al., 2016), of which only the lanthanum-modified clay Phoslock® has been used on full scale in lake restoration. Another promising product for P adsorption is the dried, amorphous ferric hydroxide (CFH-12®, Kemira, hereafter called CFH-12), which was already tested for its P binding properties in short-term exposure studies (Jørgensen et al., 2017; Lyngsie et al., 2014) and is nowadays used for arsenate and phosphate removal during drinking water treatment. However, the existing studies on P binding properties of CFH-12 have only been conducted under aerobic conditions and only for shorter exposure times of up to 2 weeks. As the high redox sensitivity of Fe seems to be by far the biggest drawback for the use of freshly formed $\text{Fe}(\text{OH})_3$, the overall aim of this study was to evaluate and compare the ability of the two compounds, CFH-12 and freshly formed $\text{Fe}(\text{OH})_3$, to reduce dissolved inorganic P (DIP) efflux in a 21-week core incubation experiment with sediments from three Danish lakes (Lake Sønderby, Lake Hampen and Lake Hostrup). The experiment was divided into an oxic (9 weeks) and an anoxic period (12 weeks) to observe the effects of microbial respiration and reducing conditions on the performance of the two compounds when being dosed relative to the mobile P pool in the sediment. This was done by monitoring dissolved nutrients, dissolved metals, and oxygen fluxes across the sediment-water interface during the incubation period. Moreover, since the long-term P sorption capacity of CFH-12 has not been studied so far, and since it has been shown that freshly formed $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ flocs lose some of their P binding capacity with ageing (Berkowitz et al., 2006; de Vicente et al., 2008; Lijklema, 1980), another aim of our study was to investigate the P binding capacity with ageing of pure phases of CFH-12 and freshly formed $\text{Fe}(\text{OH})_3$.

2. Material and methods

2.1. Study site

For the experiments, sediment and water was sampled from three shallow Danish lakes of varying alkalinity and trophic state (Supporting

information (SI) Fig. S1 and Table S1). Sediment cores ($\varnothing = 5.3$ cm; $h = 40$ cm) were sampled in clear acrylic tubes at the deepest location of each lake using a gravity core sampler. The height of the sediment column was adjusted on site to 30 cm. Bottom lake water was collected just above the sediment at the same location, whereas surface lake water was collected 10 cm below the water surface. Lake Sønderby (8 ha, 2.1 m mean depth, 5.7 m max. depth) is a hard water (3 meq L^{-1}), hypertrophic lake (average summer Secchi depth 0.7 m, chlorophyll *a* (Chl *a*) $60 \mu\text{g L}^{-1}$, average winter total P (TP) 0.22 mg P L^{-1}). Lake Hampen (76 ha, 4 m mean depth, 13.2 m max. depth) is a soft water (0.36 meq L^{-1}), oligotrophic lake (average summer Secchi depth 4.0 m, Chl *a* $7.5 \mu\text{g L}^{-1}$, average winter TP $0.015 \text{ mg P L}^{-1}$), while Lake Hostrup (210 ha, 2.1 m mean depth, 7 m max. depth) is a soft water (0.27 meq L^{-1}), eutrophic lake (average summer Secchi depth 1.1 m, Chl *a* $35 \mu\text{g L}^{-1}$, winter average TP $0.035 \text{ mg P L}^{-1}$). All three lakes experience temporary stratification and increased TP concentrations during summer due to internal P loading.

2.2. Fe products

CFH-12 is a solid granulate manufactured by Kemira (Oyj, Finland) and primarily used for the adsorption of arsenate and phosphate in drinking water. CFH-12 has a Fe content of ~44%, with 93% of the granulate having a grain size of 0.85–2 mm and 6% of smaller than 0.85 mm. The X-Ray diffraction analysis (XRD) showed that CFH-12 is an amorphous solid consisting of poorly ordered Fe oxides. Further characterization of this compound can be found in Lyngsie et al. (2014).

Freshly formed $\text{Fe}(\text{OH})_3$ was prepared by mixing $\text{FeCl}_3 \cdot 6 \text{ H}_2\text{O}$ with distilled water. Acid produced during hydrolysis of FeCl_3 was neutralized by addition of 1 M and 0.1 M NaOH to pH 6.5–7.5 in order to reduce surface charge of $\text{Fe}(\text{OH})_3$ and promote the formation of an amorphous floc. Over time, dehydration of amorphous $\text{Fe}(\text{OH})_3$ as a consequence of the crystallization process is expected, forming thermodynamically stable products such as lepidocrocite ($\gamma\text{-FeO}(\text{OH})$), goethite ($\alpha\text{-FeO}(\text{OH})$), or hematite ($\alpha\text{-Fe}_2\text{O}_3$) (von Gunten and Schneider, 1991). After horizontal agitation for 2 h, the precipitate was recovered by centrifugation and washed 3 times with distilled water before use.

2.3. CFH-12 vertical distribution in soft sediment

Since the grains of CFH-12 have a higher density than the organic-rich lake sediment, a pre-experiment was conducted to investigate the vertical distribution of CFH-12 within the sediment prior to the actual sediment core experiment (Section 2.5). For this purpose, three cores were collected from Lake Hampen in July 2014 (SI Fig. S1 and Table S1) and CFH-12 was added to the sediment surface of one core, while the other two cores served as control group. After 3 months, the sediment was sectioned in 1 cm intervals from 0 to 10 cm depth and the total sediment Fe (TFe_{sed}) was measured in each sediment layer following the procedure indicated in Section 2.5.

2.4. Ageing effect of $\text{Fe}(\text{OH})_3$ and CFH-12 on P adsorption capacity

Four different ageing/adsorption experiments were conducted in batch mode with 3 replicates per compound and treatment. In the first two experiments, (1) and (2), suspensions of freshly prepared $\text{Fe}(\text{OH})_3$ (2.3 mmol Fe) and CFH-12 (1.7 mmol Fe) were aged separately in artificial lake water (preparation see SI Table S2, final volume 500 mL, polycarbonate (PC) bottles) together with (1) 0.96 mM DIP (high P concentration) and (2) 0.05 mM DIP (low P concentration). The low P concentration in (2) resembles a DIP concentration measurable in sediment pore water in eutrophic lakes. However, P had to be added repeatedly to maintain the concentration of 0.05 mM. In both experiments, (1) and (2), DIP was measured regularly for 86 days. In experiment (3), freshly prepared $\text{Fe}(\text{OH})_3$ (2.3 mmol Fe) and CFH-12 (1.7 mmol Fe) were each stored in 30 mL artificial lake water (50 mL

centrifuge tubes) for 21 h, 1, 7, 10, 14, 56 and 113 days without any P present. After each of the indicated storing times, the suspensions were transferred into PC bottles and exposed to high P concentration (0.96 mM) for 24 h, after which DIP was measured. In experiment (4) $\text{Fe}(\text{OH})_3$ and CFH-12 suspensions were stored under similar conditions as in experiment (3) for 3 months, after which they were treated according to procedure (1) for high P exposure (0.96 mM) in ~80 days. In all cases, pH was adjusted to 6.5–7.5 by addition of 1 M and/or 0.1 M NaOH and natural movement of particles was ensured using a table shaker (Gerhardt 463727; 45 rpm, 20 °C). In order to account for possible P adsorption onto the bottle walls, the bottles were washed with distilled water and hydrochloric acid and analyzed for DIP after each experiment. However, as the amount of P adsorbed onto the bottle walls did not exceed 1% of the total P uptake, the measured values were not corrected.

2.5. Core incubation experiment

In July 2014, 14 undisturbed sediment cores were sampled at the deepest location in each lake. Bottom and surface lake water was collected from each lake at the same site and filtered through a mesh (30 μm pore size) to remove zooplankton. During transport to the laboratory, cores were kept vertical and in darkness. At the start of the experiment, two cores were sectioned into six sediment samples – 1 cm intervals from 0 to 3 cm, 2 cm intervals from 3 to 7 cm and a 3 cm section from 7 to 10 cm. A sequential extraction procedure of Paludan and Jensen (1995), modified after Psenner and Pucsko (1988), was used to define 7 sedimentary P pools: loosely adsorbed inorganic P (IP) and pore water DIP (P_{Water}), IP bound to reducible Fe (P_{BD}), IP bound to clays and Al oxides (P_{NaOH}), P bound to humic acids ($P_{\text{NaOH, Humic}}$), calcium-bound IP (P_{HCl}) and refractory organic P ($P_{\text{HCl, Res}}$). The sum of 7 different P-pools were on average 7% higher than total P values measured by hot hydrochloric acid extraction of combusted sediment. Since the single step measurement of total P (see below) is considered more accurate, the size of each P-pool was normalized to make the addition match the total P value. In each extraction, organic P was defined as the difference between total dissolved P (TDP) and DIP. Easily degradable organic P ($\text{Org-P}_{\text{labile}}$) was calculated as the sum of the organic P fraction in the first three extractions. The P pools believed to contribute to the internal P loading, the so called mobile P pool (P_{Mobile}), was calculated as the sum of P_{Water} , P_{BD} and $\text{Org-P}_{\text{labile}}$ within the upper 10 cm (e.g. Jensen et al., 2015; Reitzel et al., 2005). Total dissolved Fe (TDFe) was measured in the same extracts as P. Total sediment P (TP_{sed}) and TFe_{sed} were determined in parallel samples by combusting the sediment at 520 °C for 5 h prior to hot acid digestion with 1 M HCl. The sediment was also analyzed for dry weight (DW, %) at 105 °C for 24 h and loss on ignition (LOI, %) at 520 °C for 5 h.

The other 12 cores from each lake were divided into three different groups with 4 replicates each: one group was treated with freshly formed $\text{Fe}(\text{OH})_3$ floc ($\text{Fe}(\text{OH})_3$ treatment), the second with CFH-12 (CFH-12 treatment) and the third group served as control (control group). Both Fe compounds were mixed within the top layer of the sediment (0–3 cm) after removing the overlying water in order to obtain a ~10:1 Fe: P_{Mobile} ratio in the upper 10 cm of the sediment as minimum P trapping ratio, suggested by Jensen et al. (1992). Actual Fe additions for the $\text{Fe}(\text{OH})_3$ group were: Lake Sønderby 184 g Fe m^{-2} , Lake Hampen 91.0 g Fe m^{-2} , Lake Hostrup 50.6 g Fe m^{-2} , reaching a 10:1 Fe: P_{Mobile} molar ratio in all lakes. For the CFH-12 addition group the actual Fe additions were: Lake Sønderby 140 g Fe m^{-2} , Lake Hampen 63.3 g Fe m^{-2} , Lake Hostrup 38.5 g Fe m^{-2} , reaching a 7.6–8:1 Fe: P_{Mobile} molar ratio. The lower ratio for the CFH-12 group was caused by an initial miscalculation of the Fe content in CFH-12. After 24 h, the cores were refilled with bottom water from the respective lakes, equipped with magnetic stirring bars to ensure complete mixing of the water column and placed in the incubation tanks at constant temperature (14 °C) in a dark room. Control cores were treated similarly to the cores with added Fe. The

experimental cores were incubated for a 63-day oxic period followed by a 85-day anoxic period. During the anoxic period, the cores were N_2 -bubbled and closed with stoppers to prevent oxygenation. Before sampling, pH was measured in the water column with a probe (PHM 210 Meterlab). Samples of the water column (100 mL) were collected with syringes on days 1, 9, 22, 36, 50, 63, 78, 85, 99, 113, 134 and 148, filtered (Whatman GF/F, 0.7 μm) and preserved by addition of 2 M H_2SO_4 for the analysis of DIP, total dissolved P (TDP), Fe^{2+} and total dissolved Fe (TDFe). Sulfates (SO_4^{2-}) and nitrates (NO_3^-) were measured from day 50 onwards, while ammonium (NH_4^+) and manganese (Mn^{2+}) were only measured for the anoxic period (from day 63 onwards). DIP, Fe^{2+} and TDFe were analyzed spectrophotometrically by molybdenum blue colorimetry (Grasshoff et al., 1999) and the ferrozine method (Gibbs, 1979), respectively. TDP was measured as DIP after wet oxidation (Grasshoff et al., 1999) and dissolved organic P (DOP) was calculated as the difference between TDP and DIP. SO_4^{2-} was measured using Ion Chromatography with a conductivity cell detector (Dionex ICS 2000), NO_3^- and NH_4^+ were determined using a flow injection analyzer (Lachat Quick Chem R 8500) and Al and Mn were measured on an ICP-AES (Perkin Elmer Optima 2100 DV). Water removed by sampling was replaced with filtered (30 μm) bottom lake water (with known element concentration) up to the third sampling, after which surface lake water was used due to the high DIP concentrations in the bottom lake water. The DIP concentration in the surface water of Lake Sønderby (8 μM) was considerably higher than in the other two lakes (0.06–0.09 μM). Also, the surface water NO_3^- concentration was higher in Lake Sønderby (26 μM) and lower in Lake Hostrup (7 μM), while negligible concentrations were measured for Lake Hampen. SO_4^{2-} concentrations ranged between 0.04 and 0.05 mM.

The oxygen (O_2) consumption in the cores was calculated as the difference between the initial (previously saturated with O_2) and final O_2 concentration (mg L^{-1}) in the overlying water after 3 h of incubation at 14 °C under sealed conditions and was measured on days 33, 43 and 57 by use of a YSI oxygen meter 13F100158.

The vertical redox profile was measured on days 15, 29, 48, 61, 71, 92, 110, 132 and 146 by using a needle redox microelectrode (RD-500 μm , Unisense) connected to a mV meter (Unisense mV meter 5731). The microelectrode was inserted into the surface of the sediment down to 50 mm in 5 mm intervals. The redox potential signal was allowed to stabilize for 2 min at each depth.

Statistical analyses were performed with IBM SPSS Statistics 20 software. Statistically significant differences between treatments were assumed when $p < 0.05$ by using One-way ANOVA with Tukey HSD *post hoc* test. When normality and homogeneity of variances were still not fulfilled by transformation into logarithmic data, the non-parametric Kruskal-Wallis test was performed. Repeated measures (RM) ANOVA with the Tukey *post hoc* test were also performed to test differences in pH values between treatments at each sampling day. Sphericity assumption was fulfilled in all cases.

3. Results

3.1. CFH-12 distribution in surface sediment

The pre-experiment on the vertical distribution of CFH-12 applied to the surface sediment of a sediment core collected from Lake Hampen showed complete recovery of CFH-12 in the upper 5 cm of sediment, with the highest Fe concentration (58% of added Fe) occurring in the 2–3 cm layer (SI Fig. S2).

3.2. Organic content and Al/Fe ratio

To assess the organic matter content in the sediment we used the pool of LOI present in the top 10 cm at the beginning of the experiment. The highest LOI values were measured for Lake Hampen, followed by Lake Hostrup (0.255 and 0.242 g cm^{-2} , respectively), while Lake

Sønderby had the lowest LOI value (0.227 g cm^{-2}). For the same 10 cm sediment the total Al:Fe ratio showed the highest values for Lake Hostrup with 2.4, followed by Lake Hampen with 2.1 and Lake Sønderby with 1.9, while, if considering the P-binding forms of Al (extracted by NaOH) and Fe (extracted by BD) in the sediment surface (1 cm) Lake Hostrup has a ratio of 4.2, followed by Lake Hampen with 2.0, and Lake Sønderby with 1.3.

3.3. Sediment P and Fe pools

The contribution of each of the 7 P fractions to the average TP_{sed} in the top 10 cm of the sediment is shown in Fig. 1. The sum of the 7 P pools amounted to 121, 62 and $50 \mu\text{mol g DW}^{-1}$ in Lake Sønderby, Lake Hampen and Lake Hostrup, respectively. Lake Sønderby had the highest TP_{sed} content calculated per area for the upper 10 cm (650 mmol m^{-2}), followed by Lake Hampen and Lake Hostrup (375 and 194 mmol m^{-2} , respectively). The P_{Mobile} fraction accounted for 50% in Lake Sønderby, 41% in Lake Hampen and 45% in Lake Hostrup and decreased with depth in all three lake sediments (data not shown). The relative contribution of each P fraction to the TP_{sed} varied slightly between the lakes, but in all three lakes the largest fraction was Org- P_{Labile} (26–36% of TP_{sed}). In Lake Sønderby, the P_{BD} fraction (22% of TP_{sed}) constituted the second largest fraction, whereas P_{NaOH} , Humic (31–35% of TP_{sed}) was the second largest fraction in Lake Hampen and Hostrup.

The highest TFe_{sed} concentration in the top 10 cm (SI Fig. S3) was found in Lake Sønderby ($119 \mu\text{mol cm}^{-2}$) followed by Lake Hampen and Lake Hostrup (104 and $54.7 \mu\text{mol cm}^{-2}$, respectively), while the TFe_{sed} content was rather stable throughout the depth profile in all three lakes (data not shown). In the three lakes, most of the Fe was found in the $\text{Fe}_{\text{HCl,Res}}$ fraction (41–44% of TFe_{sed}) increasing with depth, as well as in the Fe_{BD} fraction (18–27% of TFe_{sed}) decreasing with depth (data not shown). The $\text{Fe}_{\text{BD}}:\text{P}_{\text{BD}}$ molar ratio at the start of the experiment was 2, 11.3 and 7.6 for Lake Sønderby, Lake Hampen and Lake Hostrup, respectively.

3.4. Ageing studies

Ageing of the two Fe products exposed to a high DIP concentration demonstrated that CFH-12 reached a maximum adsorption capacity of $120 \mu\text{mol P mmol}^{-1} \text{ Fe}$ after ~30 days, whereas $\text{Fe}(\text{OH})_3$ reached $180.0 \mu\text{mol P mmol}^{-1} \text{ Fe}$ after ~20 days (Fig. 2A). However, until the end of the experiment, a continuous slight increase in DIP adsorption was observed for CFH-12, implying that the maximal adsorption capacity of CFH-12 might be underestimated. The final Fe:P molar ratio after 86 days was 6.25 for $\text{Fe}(\text{OH})_3$ and 12.5 for CFH-12. During the exposure to a low and more natural DIP concentration (Fig. 2B) neither $\text{Fe}(\text{OH})_3$ nor CFH-12 reached their maximum adsorption capacity at the end of

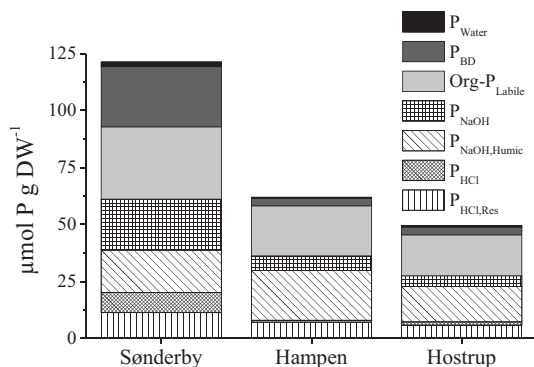


Fig. 1. P pool composition of the three different lake sediments from Lake Sønderby, Lake Hampen and Lake Hostrup calculated as average values for the top 10 cm of the sediment (initial fractionation). Shaded area accounts for P_{Mobile} pool.

the three months of exposure, until which a steady increase was observable (final adsorption CFH-12: $53.0 \mu\text{mol P mmol}^{-1} \text{ Fe}$; $\text{Fe}(\text{OH})_3$: $131 \mu\text{mol P mmol}^{-1} \text{ Fe}$). The final Fe:P molar ratio in the low exposure treatment was 25 for CFH-12 and 10 for $\text{Fe}(\text{OH})_3$.

Ageing of $\text{Fe}(\text{OH})_3$ in artificial lake water without any P present showed a 30% reduction of its short-term (24 h) DIP adsorption capacity after 113 days compared to the maximum adsorption capacity (Fig. 3A, $\text{Fe}(\text{OH})_3$ adsorption capacity after 113 days: $127 \text{ mol P mmol}^{-1} \text{ Fe}$). When exposing $\text{Fe}(\text{OH})_3$ and CFH-12 to a continuously high DIP concentration after 3 months of ageing in artificial lake water without DIP present, we observed on the one hand adsorption of DIP onto CFH-12, increasing continuously to $124 \mu\text{mol P mmol}^{-1} \text{ Fe}$ with no observable ageing effect (Fig. 3B). On the other hand we saw, that the final adsorption capacity of $145 \mu\text{mol P mmol}^{-1} \text{ Fe}$ for $\text{Fe}(\text{OH})_3$ was reached after one day. This represents a 20% reduction of the maximum adsorption capacity observed for freshly formed $\text{Fe}(\text{OH})_3$ (Figs. 2A and 3B).

3.5. Core incubation experiment

3.5.1. P effluxes

In the following paragraphs efflux of the discussed parameter is indicated with a positive value, while negative values refer to uptake of the discussed parameter. During the oxic incubation period, a significant difference emerged between the DIP efflux of the control group ($8.15 \text{ mmol P m}^{-2}$) and the $\text{Fe}(\text{OH})_3$ treatment ($-5.52 \text{ mmol P m}^{-2}$) for Lake Sønderby (Fig. 4A, $p < 0.02$), while no significant differences in DIP flux rates were observed between the three treatments in Lake Hampen or Lake Hostrup (Fig. 4B and C). In Lake Hampen, a continuous DIP uptake was found in all treatments, while Lake Hostrup showed negligible DIP release/uptake in all treatments (Fig. 4B and C, respectively).

During the anoxic incubation period, however, the differences between the treatments became more apparent. Lake Sønderby showed a significantly lower DIP release for the CFH-12 treatment ($30.9 \text{ mmol P m}^{-2}$; $p < 0.05$) and a considerable DIP uptake for the $\text{Fe}(\text{OH})_3$ treatment ($-12.3 \text{ mmol P m}^{-2}$; $p < 0.05$) compared with the control group ($54.5 \text{ mmol P m}^{-2}$), while also a comparison between $\text{Fe}(\text{OH})_3$ and CFH-12 treatment showed a significant difference ($p < 0.05$). Similarly, the control group of Lake Hostrup released significantly more DIP into the overlying water under anoxic conditions ($2.44 \text{ mmol P m}^{-2}$) compared to the CFH-12 and the $\text{Fe}(\text{OH})_3$ treatment (0.99 and $0.19 \text{ mmol P m}^{-2}$, respectively; $p \leq 0.001$ for both). In Lake Hampen, a significant decrease in DIP release during the anoxic period

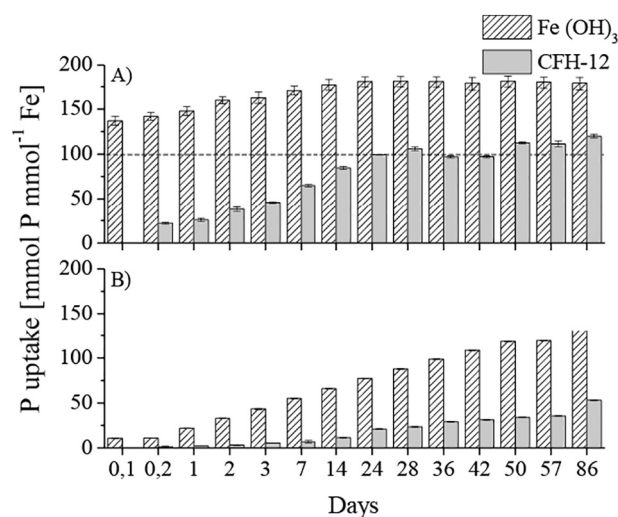


Fig. 2. Ageing effect on the adsorption of P by $\text{Fe}(\text{OH})_3$ and CFH-12 over time while being exposed to high P concentration (A) and to low P concentration (B) with continuous sampling.

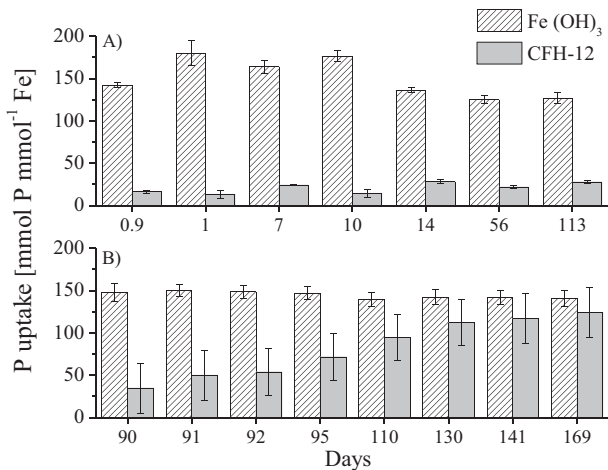


Fig. 3. A) Influence of ageing in P free artificial lake water for 0.9 to 113 days on short-term (24 h) P adsorption of CFH-12 and Fe(OH)₃ under high P exposure. B) Long-term P adsorption onto CFH-12 and Fe(OH)₃ after 3 months of ageing in P free artificial lake water and subsequent exposure to high P concentration up to 169 days.

was observed for the Fe(OH)₃ treatment ($-1.62 \text{ mmol P m}^{-2}$; $p < 0.05$) compared to the control group and CFH-12 treatment (9.19 and $2.72 \text{ mmol P m}^{-2}$, respectively). The CFH-12 treatment showed a clear tendency towards lower DIP release, although, due to the high standard deviation of the control group, no significant difference between the two groups could be observed. Overall, the addition of CFH-12 reduced the DIP release by 43% for Lake Sønderby, 70% for Lake Hampen and 59% for Lake Hostrup, corresponding to a reduction in TDP release of 39%, 66% and 55%, respectively.

Release of DOP occurred in all lakes and in all treatments during both, the oxic and the anoxic period, even during periods with DIP

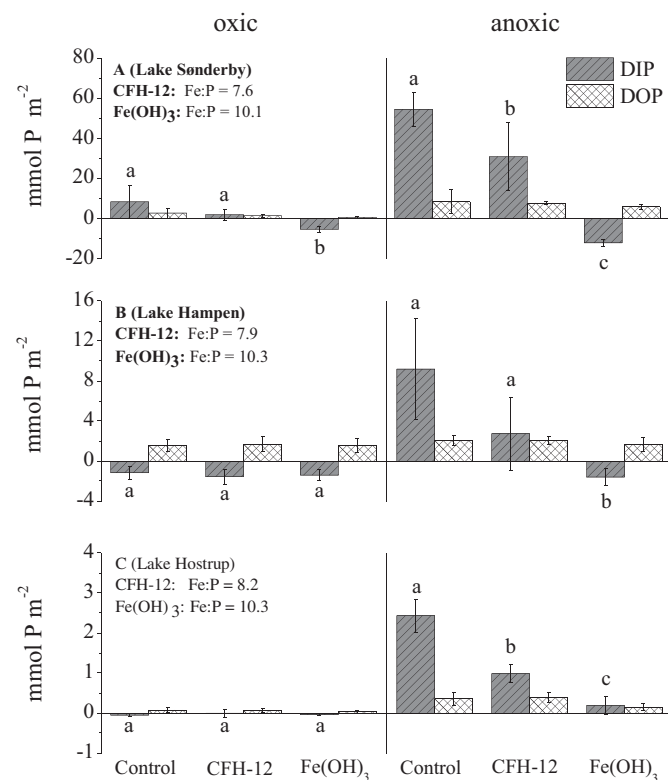


Fig. 4. Accumulated P release (DIP and DOP) from sediment cores of Lake Sønderby (A), Lake Hampen (B) and Lake Hostrup (C) during oxic (left) and anoxic (right) periods of the core incubation. Note the different scales on the ordinate axes.

uptake. In all lakes, a tendency to higher DOP release during the anoxic period was observed, but no significant differences in DOP release could be obtained between any Fe treatments in any of the lakes.

3.5.2. Fe²⁺ effluxes

Release of Fe²⁺ was in all lakes only observed in the anoxic period (Fig. 5). In Lake Sønderby, the highest Fe²⁺ release was observed for the Fe(OH)₃ treatment (Fig. 5A, 108 mmol Fe m⁻²). This was significantly higher than in the CFH-12 treatment and in the control group (50.8 and 37.9 mmol Fe m⁻², respectively; $p \leq 0.001$ for both). Similarly, Lake Hostrup showed the highest Fe²⁺ release in the Fe(OH)₃ treatment group (Fig. 5C, 69.9 mmol Fe m⁻²) compared with the control group and the CFH-12 treatment (12.9 and 10.7 mmol Fe m⁻², respectively; $p \leq 0.001$ for both). Interestingly, the Fe²⁺ release in Lake Hampen (Fig. 5B) did not demonstrate significant differences between the three treatments during the anoxic period, although also here the Fe(OH)₃ treatment had the highest Fe²⁺ release (46.9 mmol Fe m⁻²). For all lakes, the Fe³⁺ efflux was insignificant and no differences between the different treatments could be discerned (data not shown).

3.5.3. Fluxes of NO₃⁻, NH₄⁺, Mn²⁺, SO₄²⁻ and O₂

NO₃⁻, NH₄⁺ and Mn²⁺ fluxes showed considerable differences between the three lakes, but no significant differences between the treatments could be observed. The NO₃⁻ release was similar for all lakes during the oxic incubation period (10.2 to 23.7 mmol NO₃⁻ m⁻², SI Fig. S4), while during the anoxic period Lake Sønderby and Lake Hostrup demonstrated enhanced NO₃⁻ uptake (22.3 to 30.2 mmol NO₃⁻ m⁻²) compared to Lake Hampen (2.64 to 2.91 mmol NO₃⁻ m⁻²). The NH₄⁺

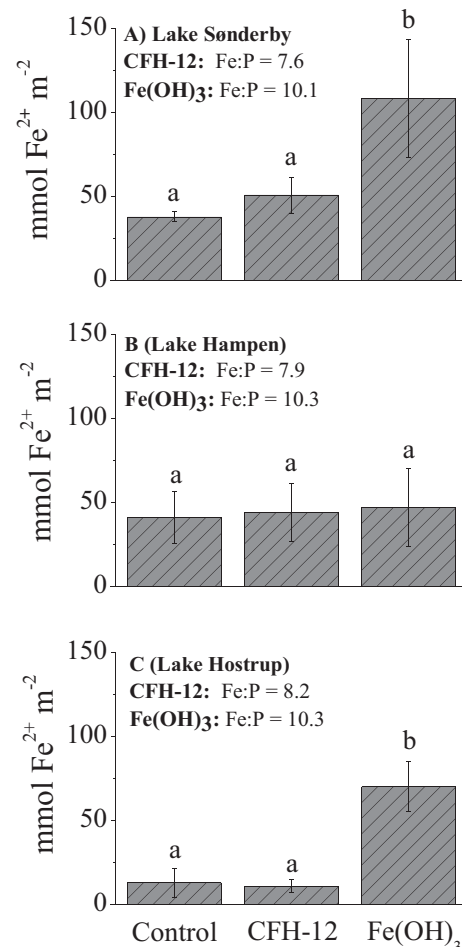


Fig. 5. Accumulated Fe²⁺ release from sediment cores of Lake Sønderby (A), Lake Hampen (B) and Lake Hostrup (C) during the anoxic period of the core incubation.

release during the anoxic period differed considerably between the lakes (SI Fig. S5). When comparing the control groups, Lake Hampen exhibited the lowest average NH_4^+ release followed by Lake Hostrup (78.8 and 115 $\text{mmol NH}_4^+ \text{ m}^{-2}$, respectively), while Lake Sønderby had a considerably higher NH_4^+ release (263 $\text{mmol NH}_4^+ \text{ m}^{-2}$). A similar trend could be observed for the Mn^{2+} release during the anoxic incubation period (SI Fig. S6) where again Lake Sønderby showed considerably higher Mn^{2+} release (15.0 to 24.7 $\text{mmol Mn}^{2+} \text{ m}^{-2}$) compared to Lake Hampen and Lake Hostrup (2.96 to 6.27 $\text{mmol Mn}^{2+} \text{ m}^{-2}$). All lakes and treatments displayed weak and similar SO_4^{2-} release during the oxic period, while the SO_4^{2-} uptake ranged from 12.8 to 42.2 $\text{mmol SO}_4^{2-} \text{ m}^{-2}$ during the anoxic period (SI Fig. S7) with no significant differences between lakes or treatments. The measurements of O_2 uptake during the oxic period revealed the highest O_2 consumption in Lake Sønderby (7.23 mol m^{-2}), while the measurements for Lake Hostrup and Lake Hampen were considerably lower (4.18 and 3.33 mol m^{-2} , respectively; SI Fig. S8). However, no significant differences appeared neither between lakes nor between treatments.

3.5.4. Redox and pH measurements

The redox profiles of the sediment cores were similar for all treatments (SI Fig. S9). However, in the oxic period, the redox potential at the sediment–water interface differed between the three lakes, where Lake Hampen and Lake Hostrup showed relatively high values (450–500 mV), while the redox potentials for Lake Sønderby were comparatively lower (320–420 mV). During the anoxic period, all three lakes had similar depth profiles in all treatments, with no steep decline in the redox potential and an average redox potential of 50–100 mV. Only the $\text{Fe}(\text{OH})_3$ treatment in Lake Sønderby showed a considerably lower redox potential with an average redox potential of -4 mV. Although the RM ANOVA analysis was statistically significant for Lake Sønderby and Hostrup (see SI Table S3, $p \leq 0.05$), pH values did not differ between treatments for any lake (see SI Fig. S10) as supported by Tukey *post hoc* test ($p > 0.05$; data not shown).

4. Discussion

4.1. Comparison of CFH-12 and freshly formed $\text{Fe}(\text{OH})_3$

In the comparison of the two iron products it should be kept in mind that the dosed Fe:P ratio was slightly lower in the CFH-12 treatment (7.6–8:1 $\text{Fe:P}_{\text{Mobile}}$ molar ratio) than in the $\text{Fe}(\text{OH})_3$ treatment (10:1 $\text{Fe:P}_{\text{Mobile}}$ ratio) in the sediment core experiment. This may act in favor of $\text{Fe}(\text{OH})_3$ when comparing the DIP effluxes from the three lake sediments. Despite this, $\text{Fe}(\text{OH})_3$ performed better than what can be explained by the modest difference in dosage. Furthermore, the higher affinity and higher P adsorption capacity of $\text{Fe}(\text{OH})_3$ were evident in the experiments with pure phases in distilled water, and even with ageing $\text{Fe}(\text{OH})_3$ performed rather well. In a similar experiment lasting 41 days, Hansen et al. (2003) also found that freshly formed FeOOH suppressed the DIP release completely under both, oxic and anoxic conditions, in mesotrophic Lake Vedsted. However, at long-term exposure, CFH-12 continuously accumulated P and the binding capacities of the two compounds became more similar. An advantage of $\text{Fe}(\text{OH})_3$ over CFH-12 is, that it reacts fast with DIP and thus is able to strip DIP from the water column. However, besides the risk of inducing pH reduction and of formation of toxic ions when adding ferrous chloride or ferric chloride to a low-alkaline lake (Bakker et al., 2016), the freshly formed $\text{Fe}(\text{OH})_3$ is also rapidly reduced in the sediment after the depletion of other quality electron acceptors such as NO_3^- and Mn^{4+} (Boström et al., 1982). This was also observed during the anoxic incubation of sediment from the two most eutrophic lakes (Lake Sønderby and Lake Hostrup). Clearly, redox potentials were low enough (<200 mV) in all cores during the anoxic period to allow Fe^{3+} reduction (Boström et al., 1982), but seemingly CFH-12 withstood reduction and dissolution much better than freshly formed $\text{Fe}(\text{OH})_3$ while still binding P in the

sediment. As judged from the very similar NH_4^+ effluxes in all treatments in any of the lakes during the anoxic incubation, the difference in Fe^{2+} effluxes cannot be explained by differences in mineralization rates, which might otherwise be expected when adding a quality electron acceptor to the sediment. Resistance to microbial reduction may be a very important feature of CFH-12 when added to lake sediments, however, full scale experiments are needed to confirm its potential for long-term P retention in anoxic sediments.

4.2. Comparison between the three lakes

While the sediment organic matter measured as LOI per area did not differ much between the three lakes the O_2 consumption likely reflected the quality of the organic matter with highest oxygen uptake in Lake Sønderby and lowest in Lake Hampen. The NO_3^- , NH_4^+ , Mn^{2+} and SO_4^{2-} fluxes also support this ranking, with Lake Sønderby having the highest rates of NO_3^- and SO_4^{2-} uptake for the oxic period and also the highest NH_4^+ and Mn^{2+} release for the anoxic period, while the corresponding uptake and release rates in Lake Hampen were the lowest. The fact that NO_3^- , NH_4^+ , Mn^{2+} and SO_4^{2-} fluxes only differed between lakes but not between treatments, indicates a negligible effect of Fe addition on them. With respect to the size of the P_{Mobile} pool, the lakes exhibit a similar ranking to that of trophic state, however, the order of the anoxic DIP release in the control treatments differs slightly between the lakes with a lower release rate in Lake Hostrup than in Lake Hampen. A likely explanation for this is that the highest Al:Fe ratio is observed in Lake Hostrup sediment both using Tal and TFe and when using the reactive forms of Al and Fe in the surface sediment. Second in ranking comes Lake Hampen and the lowest ratios are observed in Lake Sønderby. The correspondence between high Al:Fe ratios and low anoxic P-release is explained by resorption of P released from Fe by Fe-reduction onto Al ($\text{OH})_3$ present in the same depth. For P-release in the oxic period our study showed that in lakes with a $\text{Fe}_{\text{BD}}:\text{P}_{\text{BD}}$ molar ratio <8 (such as in Lake Sønderby), addition of $\text{Fe}(\text{OH})_3$ and CFH-12 resulted in suppression/reduction of DIP release from oxic sediment surfaces as a consequence of the higher P binding capacity of the sediment than in the control group. Lakes in which the $\text{Fe}_{\text{BD}}:\text{P}_{\text{BD}}$ molar ratio was close to or well above 8, such as in Lake Hampen and Hostrup, the P binding capacity of the sediment was sufficient to trap DIP under oxic conditions (Jensen et al., 1992).

4.3. Potential applicability of CFH-12 for immobilisation of P in lake sediment

The dried amorphous Fe hydroxide CFH-12 did not possess the same high affinity and adsorption capacity for DIP as the freshly formed $\text{Fe}(\text{OH})_3$. However, after 3 months of exposure to DIP in the overlying water, the adsorption capacity of CFH-12 amounted to two thirds of the DIP bound by $\text{Fe}(\text{OH})_3$ at 960 μM DIP and to one third at 50 μM DIP in the overlying water. At exposure to 960 μM DIP, CFH-12 was able to bind 66 mg P per g dry product with a molar Fe:P binding ratio of 13:1, and also during exposure to 50 μM DIP, which is a better estimation for DIP concentrations in lake sediment pore water, CFH-12 reached a binding capacity of 29 mg P per g dry product after 3 months, with a molar Fe:P binding ratio of 23:1. It is moreover noteworthy, that the DIP uptake of CFH-12 increased continuously throughout both experiments, indicating that the final binding capacity might not have been reached at the end of the experiments. In comparison, the (in Europe) commonly used lake restoration product poly-Al chloride contains 7% Al by weight (PAX XL60®, Kemira) and with a realized molar binding ratio of 10:1 (de Vicente et al., 2008), it binds 8.4 mg P per g liquid, while Phoslock®, a lanthanum modified clay, binds 10 mg P per g dry product (Reitzel et al., 2013). The product price for CFH-12 is $\sim 30\%$ higher than for poly-Al chloride per unit bound P and likely around 5 times lower than for Phoslock®. Of these products, CFH-12 is also the best suited one for low-alkaline lakes considering the risks of Al^{3+}

toxicity during the acid producing hydrolysis of Al^{3+} and liberation of potentially toxic La^{3+} ions from the clay matrix of Phoslock® at low alkalinity (Gensemer and Playle, 1999; Reitzel et al., 2017; Spears et al., 2013b). Moreover, the possibility, that the high density CFH-12 particles may sink too deep into the sediment, was investigated, and the results showed that 85% of CFH-12 added to the sediment surface of a Lake Hampen core were recovered in the upper 3 cm after 3 months and that all added CFH-12 was recovered within the upper 5 cm. Thus, CFH-12 stays at the approximately same depth as the targeted P_{Mobile} pool, and in all three lakes it suppressed the anoxic DIP release from the sediment during the 148-day core incubation experiment. In addition, Fe^{2+} was seemingly not released from the sediments treated with CFH-12 under anaerobic conditions as otherwise observed for iron from freshly formed $\text{Fe}(\text{OH})_3$.

5. Conclusion

Our results suggest that CFH-12 binds P relatively well over time under both, oxic and anoxic conditions, and equally well in hard water and soft water lakes. Use of the product poses little to no risk of toxicity and product costs are only 30% higher than the costs for poly-Al chloride, which may in return be balanced by less transport costs due to a higher P binding per unit product. Thus, CFH-12 holds promising potential as a P binding agent in soft water lakes. Full-scale testing is, however, needed before its use can be unconditionally recommended.

Funding

The study was supported by Junta de Andalucía (project P10-RNM-6630, Spain), MINECO CTM (project 2013-46951-R, Spain) and by the European Regional Development Fund (ERDF). Funding was also obtained from the Danish Centre for Lake Restoration (a Villum Centre of Excellence).

Acknowledgments

We thank Carina Lohman and Rikke Holm for assistance with sampling and analyses.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.02.059>.

References

- Bakker, E.S., van Donk, E., Immers, A.K., 2016. Lake restoration by in-lake iron addition: a synopsis of iron impact on aquatic organisms and shallow lake ecosystems. *Aquat. Ecol.* 50:1–15. <https://doi.org/10.1007/s10452-015-9552-1>.
- Berkowitz, J., Anderson, M.A., Amrhein, C., 2006. Influence of aging on phosphorus sorption to alum floc in lake water. *Water Res.* 40:911–916. <https://doi.org/10.1016/j.watres.2005.12.018>.
- Boström, B., Jansson, M., Forsberg, C., 1982. Phosphorus release from lake sediments. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* 18, 5–59.
- Copetti, D., Finsterle, K., Marziali, L., Stefani, F., Tartari, G., Douglas, G., Reitzel, K., Spears, B.M., Winfield, I.J., Crosa, G., D'Haese, P., Yasseri, S., Lürling, M., 2016. Eutrophication management in surface waters using lanthanum modified bentonite: a review. *Water Res.* 1–13. <https://doi.org/10.1016/j.watres.2015.11.056>.
- Correll, D.L., 1998. The role of phosphorus in eutrophication of receiving waters: a review. *J. Environ. Qual.* 27:261–266. <https://doi.org/10.2134/jeq1998.00472425002700020004x>.
- Funes, A., de Vicente, J., Cruz-Pizarro, L., Álvarez-Manzaneda, I., de Vicente, I., 2016. Magnetic microparticles as a new tool for lake restoration: a microcosm experiment for evaluating the impact on phosphorus fluxes and sedimentary phosphorus pools. *Water Res.* 89:366–374. <https://doi.org/10.1016/j.watres.2015.11.067>.
- Gensemer, R.W., Playle, R.C., 1999. The bioavailability and toxicity of aluminum in aquatic environments. *Crit. Rev. Environ. Sci. Technol.* 29 (4):315–450. <https://doi.org/10.1080/10643389991259245>.

- Gibbs, M.M., 1979. A simple method for the rapid determination of iron in natural waters. *Water Res.* 13:295–297. [https://doi.org/10.1016/0043-1354\(79\)90209-4](https://doi.org/10.1016/0043-1354(79)90209-4).
- Grasshoff, K., Kremling, K., Ehrhardt, M., 1999. *Methods of Seawater Analysis*. 3rd ed. Wiley-VCH, pp. 159–228 (ISBN 3-527-29589-5).
- von Gunten, U., Schneider, W., 1991. Primary products of the oxygenation of iron (II) at an oxic-anoxic boundary: nucleation, aggregation, and aging. *J. Colloid Interface Sci.* 145, 127–139.
- Hansen, J., Reitzel, K., Jensen, H.S., Andersen, F., 2003. Effects of aluminum, iron, oxygen and nitrate additions on phosphorus release from the sediment of a Danish softwater lake. *Hydrobiologia* 492:139–149. <https://doi.org/10.1023/A:1024826131327>.
- Hupfer, M., Lewandowski, J., 2008. Oxygen controls the phosphorus release from lake sediments – a long-lasting paradigm in limnology. *Int. Rev. Hydrobiol.* 93:415–432. <https://doi.org/10.1002/iroh.200711054>.
- Huser, B.J., Egemose, S., Harper, H., Hupfer, M., Jensen, H., Pilgrim, K.M., Reitzel, K., Rydin, E., Futter, M., 2015. Longevity and effectiveness of aluminum addition to reduce sediment phosphorus release and restore lake water quality. *Water Res.* 1–11. <https://doi.org/10.1016/j.watres.2015.06.051>.
- Jaeger, D., 1994. Effects of hypolimnetic water aeration and iron-phosphate precipitation on the trophic level of Lake Krupunder. *Hydrobiologia* 275–276:433–444. <https://doi.org/10.1007/BF00026732>.
- Jensen, H.S., Kristensen, P., Jeppesen, E., Skytthe, E.A., 1992. Iron:phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. *Hydrobiologia* 235–236:731–743. <https://doi.org/10.1007/BF00026261>.
- Jensen, H.S., Reitzel, K., Egemose, S., 2015. Evaluation of aluminum treatment efficiency on water quality and internal phosphorus cycling in six Danish lakes. *Hydrobiologia*: 189–199. <https://doi.org/10.1007/s10750-015-2186-4>.
- Jørgensen, C.A., Jensen, H.S., Egemose, S., 2017. Phosphate adsorption to iron sludge from waterworks, ochre precipitation basins and commercial ferrihydrite at ambient freshwater phosphate concentrations. *Environ. Technol.* 38:2185–2192. <https://doi.org/10.1080/09593330.2016.1250819>.
- Kleeberg, A., Herzog, C., Hupfer, M., 2013. Redox sensitivity of iron in phosphorus binding does not impede lake restoration. *Water Res.* 47:1491–1502. <https://doi.org/10.1016/j.watres.2012.12.014>.
- Lijklema, L., 1980. Interaction of orthophosphate with iron (III) and aluminum hydroxides. *Environ. Sci. Technol.* 14, 537–541.
- Lyngsø, G., Borggaard, O.K., Hansen, H.C.B., 2014. A three-step test of phosphate sorption efficiency of potential agricultural drainage filter materials. *Water Res.* 51:256–265. <https://doi.org/10.1016/j.watres.2013.10.061>.
- Paludan, C., Jensen, H.S., 1995. Sequential extraction of phosphorus in freshwater wetland and lake sediment: significance of humic acids. *Wetlands* 15:365–373. <https://doi.org/10.1007/BF03160891>.
- Psenner, R., Pucsko, R., 1988. Phosphorus fractionation: advantages and limits of the method for the study of sediment P origins and interactions. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* 30, 43–59.
- Reitzel, K., Hansen, J., Andersen, F.Ø., Hansen, K.S., Jensen, H.S., 2005. Lake restoration by dosing aluminum relative to mobile phosphorus in the sediment. *Environ. Sci. Technol.* 39, 4134–4140.
- Reitzel, K., Andersen, F.Ø., Egemose, S., Jensen, H.S., 2013. Phosphate adsorption by lanthanum modified bentonite clay in fresh and brackish water. *Water Res.* 47:2787–2796. <https://doi.org/10.1016/j.watres.2013.02.051>.
- Reitzel, K., Balslev, K.A., Jensen, H.S., 2017. The influence of lake water alkalinity and humic substances on particle dispersion and lanthanum desorption from a lanthanum modified bentonite. *Water Res.* 125:191–200. <https://doi.org/10.1016/j.watres.2017.08.044>.
- Rothe, M., Frederichs, T., Eder, M., Kleeberg, A., Hupfer, M., 2014. Evidence for vivianite formation and its contribution to long-term phosphorus retention in a recent lake sediment: a novel analytical approach. *Biogeosciences* 11:5169–5180. <https://doi.org/10.5194/bg-11-5169-2014>.
- Schindler, D.W., Carpenter, S.R., Chapra, S.C., Hecky, R.E., Orihel, D.M., 2016. Reducing phosphorus to curb Lake eutrophication is a success. *Environ. Sci. Technol.* 2016 (50):8923–8929. <https://doi.org/10.1021/acs.est.6b02204>.
- Søndergaard, M., Jensen, J.P., Jeppesen, E., 2003. Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia* 506–509:135–145. <https://doi.org/10.1023/B:HYDR.0000008611.12704.dd>.
- Spears, B.M., Dudley, B., Reitzel, K., Rydin, E., 2013a. Geo-engineering in lakes—a call for consensus. *Environ. Sci. Technol.* 47:3953–3954. <https://doi.org/10.1021/es401363w>.
- Spears, B.M., Lürling, M., Yasseri, S., Castro-Castellon, A.T., Gibbs, M., Meis, S., McDonald, C., McIntosh, J., Sleep, D., Van Oosterhout, F., 2013b. Lake responses following lanthanum-modified bentonite clay (Phoslock®) application: an analysis of water column lanthanum data from 16 case study lakes. *Water Res.* 47:5930–5942. <https://doi.org/10.1016/j.watres.2013.07.016>.
- Su, Y., Cui, H., Li, Q., Gao, S., Ku, J., 2013. Strong adsorption of phosphate by amorphous zirconium oxide nanoparticles. *Water Res.* 47 (14):5018–5026. <https://doi.org/10.1016/j.watres.2013.05.044>.
- de Vicente, I., Huang, P., Andersen, F., Jensen, H.S., 2008. Phosphate adsorption by fresh and aged aluminum hydroxide. Consequences for lake restoration. *Environ. Sci. Technol.* 42:6650–6655. <https://doi.org/10.1021/es800503s>.
- de Vicente, I., Merino-Martos, A., Cruz-Pizarro, L., de Vicente, J., 2010. On the use of magnetic nano and microparticles for lake restoration. *J. Hazard. Mater.* 181:375–381. <https://doi.org/10.1016/j.jhazmat.2010.05.020>.