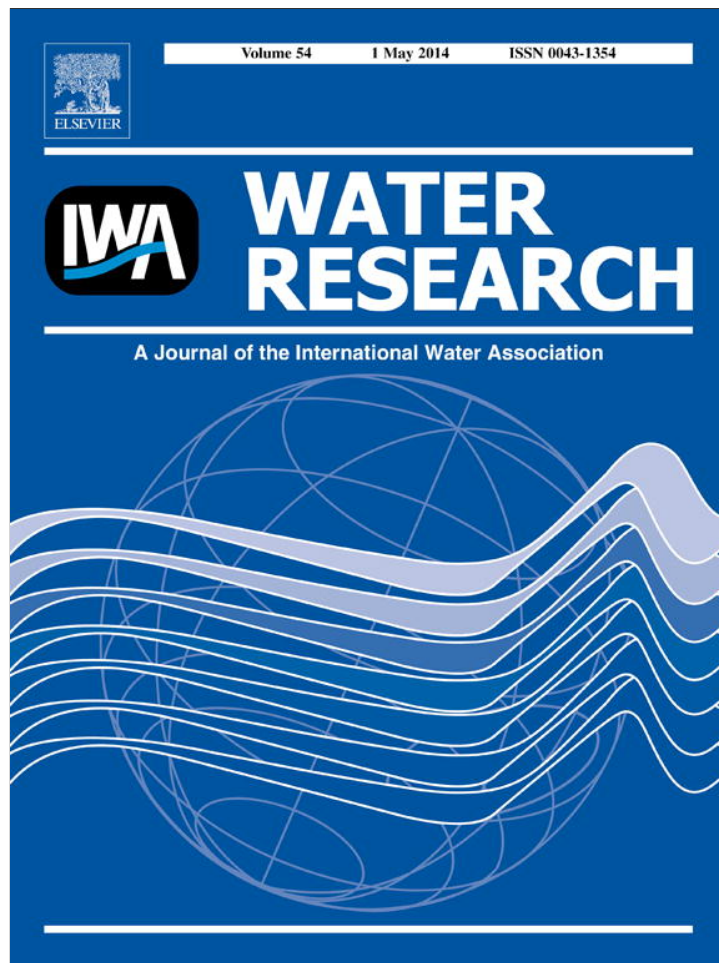


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

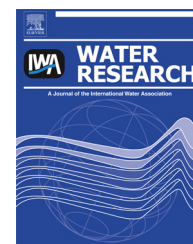
Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/authorsrights>

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Humic substances interfere with phosphate removal by lanthanum modified clay in controlling eutrophication

Miquel Lüring^{a,b,*}, Guido Waajen^{a,c}, Frank van Oosterhout^a

^a Aquatic Ecology & Water Quality Management Group, Department of Environmental Sciences, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands

^b Department of Aquatic Ecology, Netherlands Institute of Ecology (NIOO-KNAW), P.O. Box 50, 6700 AB Wageningen, The Netherlands

^c Regional Water Authority Brabantse Delta, P.O. Box 5520, 4801 DZ Breda, The Netherlands

ARTICLE INFO

Article history:

Received 10 November 2013

Received in revised form

21 January 2014

Accepted 25 January 2014

Available online 5 February 2014

Keywords:

DOC

Eutrophication control

Lake management

Lake restoration

Lanthanum modified clay

Phoslock[®]

ABSTRACT

The lanthanum (La) modified bentonite Phoslock[®] has been proposed as dephosphatisation technique aiming at removing Filterable Reactive Phosphorus (FRP) from the water and blocking the release of FRP from the sediment. In the modified clay La is expected the active ingredient. We conducted controlled laboratory experiments to measure the FRP removal by Phoslock[®] in the presence and absence of humic substances, as La complexation with humic substances might lower the effectiveness of La (Phoslock[®]) to bind FRP. The results of our study support the hypothesis that the presence of humic substances can interfere with the FRP removal by the La-modified bentonite. Both a short-term (1 d) and long-term (42 d) experiment were in agreement with predictions derived from chemical equilibrium modelling and showed lower FRP removal in presence of humic substances. This implies that in DOC-rich inland waters the applicability of exclusively Phoslock[®] as FRP binder should be met critically. In addition, we observed a strong increase of filterable La in presence of humic substances reaching in a week more than 270 $\mu\text{g La l}^{-1}$ that would infer a violation of the Dutch La standard for surface water, which is 10.1 $\mu\text{g La l}^{-1}$. Hence, humic substances are an important factor that should be given attention when considering chemical FRP inactivation as they might play a substantial role in lowering the efficacy of metal-based FRP-sorbents, which makes measurements of humic substances (DOC) as well as controlled experiments vital.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Eutrophication through excessive nutrient enrichment is considered the most important water quality problem in

freshwater and coastal ecosystems (Conley et al., 2009; Smith and Schindler, 2009). Water blooms of potentially toxic cyanobacteria (blue-green algae) – the most obvious symptoms of eutrophication, are a threat to human and animal health

* Corresponding author. Aquatic Ecology & Water Quality Management Group, Department of Environmental Sciences, Wageningen University, Droevendaalsesteeg 3a, 6708 PB Wageningen, The Netherlands. Tel.: +31 317 483898; fax: +31 317 419000.

E-mail address: miquel.lurling@wur.nl (M. Lüring).

(Codd et al., 2005; Dittmann and Wiegand, 2006), e.g. they cause swimming bans, and have caused drinking water shortages (Lürding and Van Oosterhout, 2013a; Yang and Liu, 2010). The attainment of a good water quality is required by European legislation (EU, 2000) and the 'good ecological state' or 'potential' of lakes by 2015, as required from the EU WFD (European Union, 2000), makes eutrophication control an important challenge to water authorities.

It is widely accepted that excessive loadings with both nitrogen and phosphorus, are the major causes of blooms of cyanobacteria (Smith et al., 1999; Cooke et al., 2005), which would indicate that mitigation should focus on dual reductions (Paerl, 2009). For practical purposes only phosphorus can be lowered effectively to limiting concentrations, hence eutrophication control has primarily focused on phosphorus control (Schindler et al., 2008). Phosphorus control implies both strong reduction of the external phosphorus inputs as well as phosphorus present within the system (Klapper, 2003; Cooke et al., 2005; Mehner et al., 2008). In-lake phosphorus control requires both water column dephosphatisation as well as blocking phosphorus release from the sediment (Cooke et al., 1993, 2005; Spears et al., 2013a). Traditionally, aluminium-, calcium- and iron salts have been applied for in-lake restoration (e.g. Cooke et al., 1993; Cooke et al., 2005), while more recently solid-phase phosphorus sorbents have gained interest (Spears et al., 2013a). Solid-phase phosphorus sorbents are mainly clays enriched with aluminium (Al) (Gibbs et al., 2011), iron (Fe) (Zamparas et al., 2012) or lanthanum (La) (Haghseresht et al., 2009; Yuan et al., 2009).

Most information exists on the La modified bentonite Phoslock[®] (Douglas, 2002). Phoslock[®] was developed by the Australian CSIRO, as dephosphatisation technique aiming at removing Filterable Reactive Phosphorus (FRP) from the water and blocking the release of FRP from the sediment. Several studies reported Phoslock[®] as promising technique to control eutrophication (Robb et al., 2003; Akhurst et al., 2004; Ross et al., 2008; Haghseresht et al., 2009; Van Oosterhout and Lürding, 2013). Under favourable conditions La and FRP bind to rhabdophane (LaPO₄), a mineral with an extreme low solubility ($K_{sp} = 10^{-24.7}$ to $10^{-25.7} \text{ mol}^2 \text{ l}^{-2}$) (Johannesson and Lyons, 1994; Liu and Byrne, 1997). The La-FRP bond is less affected by non-neutral pH as compared with Al- and Fe-based FRP binders (Douglas et al., 2004). The FRP binding capacity of La is not affected by altered redox conditions such as those in anoxic waters (Ross et al., 2008). However, the efficacy of this La modified clay in controlling phosphorus in an enclosure experiment (Lürding and Faassen, 2012) and in the first application in The Netherlands (Het Groene Eiland) did not meet the expectations (Lürding and Van Oosterhout, 2013a). Recent experiments showed that the dose of 100:1 Phoslock[®]:P as recommended by the manufacturers was too low (Reitzel et al., 2013a,b).

The effectiveness of La to bind FRP is hindered by naturally occurring compounds such as humic substances. Although it is plausible that naturally occurring oxyanions (in particular carbonates) hinder this effectiveness as well (Johannesson and Lyons, 1994), we focus on humic substances because the actual DOC concentrations in many (Dutch) lakes (e.g. 2–20 mg l⁻¹; De Lange, 2000) are in the range where a reduction of the effectiveness might be expected. Complex-formation of La with humic substances was predicted at 5 mg l⁻¹ DOC (Tang and

Johannesson, 2003) and experimentally demonstrated for example at 10 mg l⁻¹ Aldrich humic acids, natural organic matter and Suwannee River fulvic acids (Sonke and Salters, 2006; Tang and Johannesson, 2010a,b). Chemical equilibrium modelling suggested that La complexation with humic substances is dominated by humic complexes from pH 4 upward (Sonke, 2006). It is suggested that humic substances may have caused the La-modified bentonite clay (LMB) to be less effective than theoretically expected (Lürding and Faassen, 2012; Lürding and Van Oosterhout, 2013a; Reitzel et al., 2013b), i.e. through the formation of complexes, the humic substances physically hinder the precipitation of La with FRP. Humic substances are known to form complexes with metals (Van Dijk, 1971; Rashid, 1974) and as such could potentially reduce the P-removal capacity of the LMB. This is an important notion as eutrophic/dystrophic lakes tend to have higher DOC concentrations (on average 10–30 mg l⁻¹) than oligo/mesotrophic ones (on average 2–3 mg l⁻¹) (Thurman, 1985). Furthermore, climate change is predicted to increase leakage of terrestrial humic substances to surface waters leading to "brownification" (Monteith et al., 2007; Ekvall et al., 2013). Hence, the potential effect of humic substances on the efficacy of La modified clay for eutrophication control should be taken into consideration. To our knowledge no controlled experiments testing the effect of humic substances on the FRP removal by the LMB have been reported in the scientific literature. As we suspected humic substances to interfere with the FRP binding capacity of LMB, we conducted controlled laboratory experiments to measure the FRP removal by the LMB in the presence and absence of humic substances. We tested the hypotheses that the presence of humic substances influences the FRP removal of the LMB and that this influence depends on humic substance concentration.

2. Materials and methods

2.1. Chemicals

The lanthanum modified bentonite, LMB, (Phoslock[®], alleged 5% La) was supplied by Phoslock Europe GmbH (Ottersberg, Germany). Humic substance was obtained from Sigma–Aldrich[®] Chemie GmbH (Steinheim, Germany) as humic acid sodium salt, technical grade (CAS: 68131-04-4). Dipotassium hydrogen phosphate (CAS: 7758-11-4) was obtained from Merck KGaA (product no. 1.05104.1000, Darmstadt, Germany).

2.2. Chemical equilibrium modelling

The effect of humic substances on the P-removal efficiency of Phoslock[®] was evaluated by chemical equilibrium modelling using the program CHEAQS Pro (release P2013.1; Verweij, 2013). In this program Model V/WHAM-W (Tipping and Hurley, 1992; Tipping, 1994) was chosen to evaluate the formation of complexes of lanthanum with humic acids. Model V/WHAM-W is a discrete site model for humic-ion complexation using carboxylic and phenolic groups as two main types of functional groups (Sonke, 2006). The model was run with: 2182 µg l⁻¹ La (based on 50 mg l⁻¹ Phoslock[®] containing 4.37% La that was determined by ICP-MS in five different batches of

Phoslock[®]; $43656 \pm 1567 \text{ mg kg}^{-1}$ and assuming all La in the clay is available to bind FRP), $595 \mu\text{g l}^{-1}$ FRP at pH = 7 and pH = 8 and varying humic substances concentrations as DOC (0, 2, 4, 6, 8, 10, 12 and 14 mg l^{-1}). The proportion of humic acids and fulvic acids was set at 100% HA – 0% FA and 50% HA – 50% FA. The La:P ratio modelled was comparable to the ones used in the experiments.

2.3. Short-term (24 h) P-removal experiment

A short term (24 h) controlled experiment was done to test the FRP-removal by Phoslock[®] in a standard FRP-solution at different concentrations of humic substances. The experiment consisted of two series (one without and one with Phoslock[®]), eight DOC concentrations (0, 2, 4, 6, 8, 10, 12 and 14 mg DOC l^{-1}) and three replicates, yielding $2 \times 8 \times 3 = 48$ experimental units. Humic substances were dissolved in purified water (Q-Pod, Millipore) in triplicate in the concentration range 0, 1, 5, 10, 50, 100 and 1000 mg l^{-1} . The concentrations of the humic substance in the solutions were determined as DOC by a Shimadzu TOC analyzer at the Chemical–Biological Soil Laboratory of the Department of Soil Sciences (Wageningen University, The Netherlands). Below humic substance concentrations are referred to as DOC (mg l^{-1}) concentrations. Two 2.5 l stock solutions with a nominal FRP concentration of $600 \mu\text{g l}^{-1}$ (measured $595 \mu\text{g FRP l}^{-1}$) were made by dissolving K_2HPO_4 in purified water (Q-Pod, Millipore). To one of the stocks humic substances was added at 14 mg DOC l^{-1} . Aliquots of both stocks were distributed over 48 glass tubes of 125 ml such that six replicate tubes contained a total volume of 100 ml with different concentrations of humic substances (0, 2, 4, 6, 8, 10, 12 and 14 mg DOC l^{-1}). Then these series were split in two such that three replicates of each DOC concentration were treated with Phoslock[®] dosed at approximate 50 mg l^{-1} and the other three left untreated. The Phoslock[®] was added by making a slurry with water from the designated tubes and adding it quantitatively at the surface of the tubes. The tubes were placed for 24 h in the dark at room temperature ($\sim 22 \text{ }^\circ\text{C}$) without agitation, where after subsamples were filtered through $0.45 \mu\text{m}$ membrane filters (Whatman NC45) and analysed on their FRP concentration on a Skalar SAN+ segmented flow analyser following the Dutch standard NEN 6663 (NNI, 1986). The pH and electric conductivity (EC, $\mu\text{S cm}^{-1}$) were determined in an additional series to avoid disturbance in the experimental tubes using a WTW Multi 3500i meter.

The intended statistical test for the residual FRP concentrations was a two-way ANOVA based on the factorial design with different DOC concentrations in absence/presence of Phoslock[®]. However, because the Normality Test (Shapiro–Wilk) failed ($P < 0.050$) and data transformation appeared insufficient, FRP concentrations in the control series and the Phoslock[®] series were tested against each other using Parallel Lines Analysis in the tool pack SigmaPlot version 12.3. This analysis compared the slopes and intercepts of the regression lines of FRP concentrations at different DOC concentrations in absence and presence of Phoslock[®]. Similarly, the effect of DOC on the pH and EC in absence and presence of Phoslock[®] was evaluated by Parallel Lines Analysis (SigmaPlot version 12.3).

Chemical equilibrium modelling (CHEAQS Pro release P2013.1; Verweij, 2013) was done to estimate the theoretical residual FRP concentrations in the standard P-solution at different concentration of humic substances in absence and presence of La. In this model it is assumed that all La in Phoslock[®] is available to FRP binding as is suggested from information provided by the manufacturer (<http://www.phoslock.eu/en/phoslock/about-phoslock/>; last accessed January 21st 2014). The input values for the model were derived from the measured FRP concentration in controls (without Phoslock[®]), the concentration of La added ($2182 \mu\text{g l}^{-1}$), the added DOC concentration (0, 2, 4, 6, 8, 10, 12 and 14 mg DOC l^{-1}) as 100% humic acids and measured pH values. The slopes and intercepts of the regression lines were compared using Parallel Lines Analysis (SigmaPlot version 12.3).

2.4. Long-term (6 week) P-removal experiment

The effect of humic substances on the FRP-removal efficiency by Phoslock[®] was tested in a 6 weeks controlled experiment. A stock solution of $600 \mu\text{g FRP l}^{-1}$ was made by dissolving K_2HPO_4 in purified water. Six cylinders were filled with 1 l of the stock solution, to three cylinders humic substances were added at 10 mg DOC l^{-1} , where after all cylinders were treated with 50 mg l^{-1} Phoslock[®]. The cylinders were covered and placed in the laboratory in the dark ($\sim 22 \text{ }^\circ\text{C}$). After 1 h, 1 day, 3 days, 1 week, 2, 4 and 6 weeks 30 ml subsamples were filtered through $0.45 \mu\text{m}$ membrane filters (Whatman NC45). Of these 20 ml was used for measurement of their FRP concentration on a Skalar SAN+ segmented flow analyser following the Dutch standard NEN 6663 (NNI, 1986). The remaining 10 ml was acidified with $100 \mu\text{l}$ 7 M HNO_3 and subsequently the La content was determined by ICP-MS in the Chemical–Biological Soil Laboratory of the Department of Soil Sciences (Wageningen University).

The FRP and La concentrations were statistically evaluated by repeated measure ANOVAs (IBM[®] SPSS[®] Statistics version 19.0.0.1). The data were checked for normality using Shapiro–Wilk test of Normality. The non-significance indicated data fitted the normal curve well, while Mauchly's test indicated that the assumption of sphericity had not been violated.

Chemical equilibrium modelling (CHEAQS Pro release P2013.1; Verweij, 2013) was done to estimate theoretical residual FRP concentrations in the Phoslock[®] treated P-solutions without and with humic substances (10 mg DOC l^{-1}). The pH of both solutions was measured in a series of 4 cylinders without and 4 with 10 mg DOC l^{-1} , yielding mean pH = 6.9 and pH = 7.6 in controls and DOC treatments, respectively, that were used as input in the model.

3. Results

3.1. Chemical equilibrium modelling

The chemical equilibrium modelling indicated no effect of humic substances (i.e. DOC) on residual FRP concentrations in the absence of La. Simulating a Phoslock[®] treatment (adding

La) pointed out that in the absence of humic substances all La precipitated with FRP. Because La was somewhat under dosed to FRP, the percentage P as LaPO_4 is not 100%, but 81.7% which is the maximum based on available La (Fig. 1A). Simulating increasing concentrations of humic substances (DOC) reduced FRP binding by La, in which the reduction depended on DOC concentrations (Fig. 1A). Furthermore, the modelling indicated an interactive effect of pH and composition of the humic substances, i.e. humic and fulvic acids (Fig. 1A). Over all, in the presence of humic substances, FRP binding by La is lower at pH = 8 than it is at pH = 7. In case 50% of the humic substances were present as FA, FRP binding by La was less than in the absence (0%) of FA. This modelled reduction in LaPO_4 precipitation seemed to be caused by formation of complexes of La with humic acids (Fig. 1B).

3.2. Short-term (24 h) P-removal experiment

Adding DOC to the control (FRP solutions) or Phoslock® series (FRP solution + Phoslock® added) resulted in a linear increase in pH and EC. The slopes of these increases were similar (Table 1). In the Phoslock® series the intercept of EC was significantly higher than in de control (Table 1).

The residual FRP concentration in the control series remained approximately $600 \mu\text{g l}^{-1}$ (Fig. 2A). In the Phoslock® series the residual FRP concentrations were lower than in the controls, but tended to increase with higher DOC concentrations (Fig. 2A). The Parallel Line Analysis revealed that the slopes of regressions in control series and Phoslock® treatments were significantly different ($F_{1,12} = 17.97$; $P = 0.001$).

The residual FRP was higher – and thus the reduction in FRP was less – than predicted from the amount of Phoslock® added. In the absence of DOC the addition of Phoslock® could

have reduced FRP from 595 to $108 \mu\text{g l}^{-1}$ – only a reduction to $333 \mu\text{g l}^{-1}$ was measured (Fig. 2B). Parallel Line Analysis of measured and modelled FRP concentrations revealed that the slopes of their regression lines were similar ($F_{1,12} = 0.72$; $P = 0.412$), but that the intercepts were significantly different ($F_{1,13} = 218.4$; $P < 0.001$). The measured reduction of the FRP-binding efficiency by Phoslock® is in agreement with the predictions from chemical equilibrium modelling. However, the magnitude of FRP-removal after 24 h is far lower than expected (Fig. 2B).

3.3. Long-term (6 week) P-removal experiment

In the absence of DOC the model predicted La binding to result in a residual FRP of $68 \mu\text{g l}^{-1}$, while in the presence of DOC the model predicted a residual FRP concentrations of $152 \mu\text{g l}^{-1}$ (Fig. 3). The measured residual FRP concentration in the absence DOC (controls) gradually decreased towards this predicted value and levelled off around $90 \mu\text{g l}^{-1}$ (Fig. 3). In contrast, in the presence of 10 mg DOC l^{-1} residual FRP concentrations levelled off around $230 \mu\text{g l}^{-1}$, which is 2.5 times more than the expected concentration assuming no interference from DOC (Fig. 3). The repeated measure ANOVA revealed that in both treatments the FRP concentrations decreased significantly over time ($F_{6,24} = 1585$; $P < 0.001$). However, in the presence of DOC the residual FRP concentrations were significantly higher than in their absence ($F_{1,4} = 161.5$; $P < 0.001$). The course of the decline of FRP concentrations in controls deviated significantly from those in the DOC treatments ($F_{6,24} = 24.9$; $P < 0.001$).

The filterable La concentration in the sole Phoslock® series (controls) reached $3.3 \mu\text{g l}^{-1}$ after one day and then gradually decreased to $<0.2 \mu\text{g l}^{-1}$ at the end of the experiment. In contrast, in presence of DOC filterable La concentrations

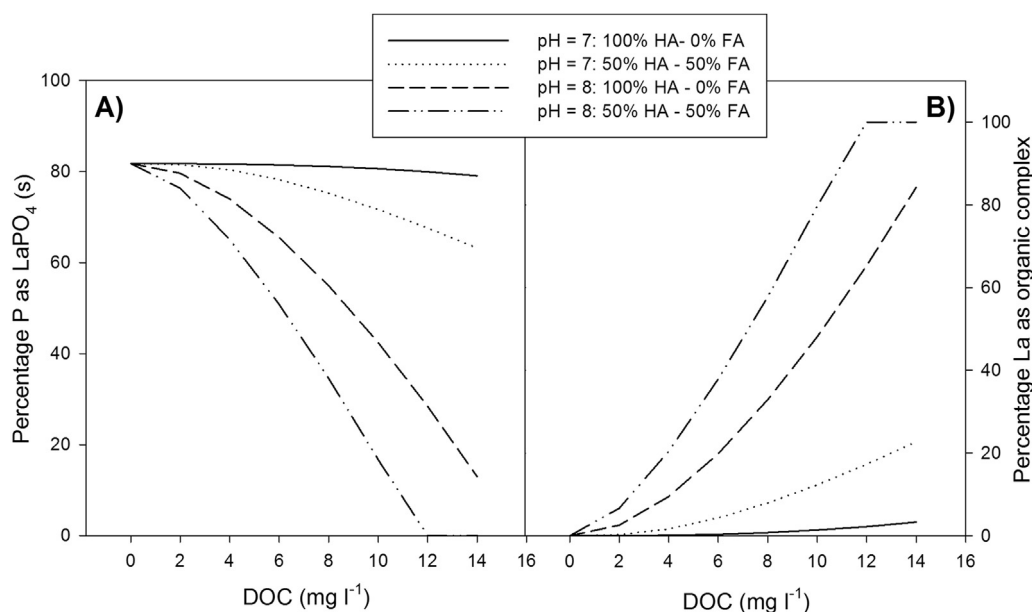


Fig. 1 – Proportions of phosphorus as rhabdophane (LaPO_4 , Panel A) and lanthanum (La) speciation as humic complexes (Panel B) under two pH (7 and 8) and two humic acid (HA) – fulvic acid (FA) scenarios (100% HA – 0% FA; 50% HA – 50% FA) as predicted from chemical equilibrium modelling in waters varying in humic acid concentration (as DOC) from 0 to 14 mg l^{-1} .

Table 1 – Results of linear regressions of pH and electric conductivity (EC, $\mu\text{S cm}^{-1}$) against different DOC concentrations (0–14 mg l^{-1}) in FRP solutions (0.6 mg FRP l^{-1}) and FRP solutions with 50 $\text{mg Phoslock}^{\circledR} \text{l}^{-1}$ added, including r_{adj}^2 of the fits and F- and P-values of comparison of slopes and intercepts of the regressions.

	pH	EC
FRP solution	$\text{pH} = 6.445 + (0.100 \times \text{DOC})$ $r_{\text{adj}}^2 = 0.973$	$\text{EC} = 983.750 + (100.193 \times \text{DOC})$ $r_{\text{adj}}^2 = 0.963$
FRP + Phoslock [®]	$\text{pH} = 6.621 + (0.0877 \times \text{DOC})$ $r_{\text{adj}}^2 = 0.955$	$\text{EC} = 1161.667 + (91.190 \times \text{DOC})$ $r_{\text{adj}}^2 = 0.988$
Equality of slopes	$F_{1,12} = 1.69$; $P = 0.218$	$F_{1,12} = 1.17$; $P = 0.300$
Equality of intercepts	$F_{1,13} = 4.08$; $P = 0.065$	$F_{1,13} = 8.97$; $P = 0.001$

increased sharply to 273 $\mu\text{g l}^{-1}$ within a week (Fig. 4). Samples in presence of DOC taken after 2, 4 and 6 weeks showed precipitation in filtrates and were therefore excluded from analysis.

4. Discussion

The results of our study support the hypothesis that DOC can interfere with the FRP removal by the lanthanum-modified bentonite. Both a short-term (1 d) and long term (42 d) experiment were in agreement with predictions derived from chemical equilibrium modelling and showed lower FRP removal in presence of humic substances. However in our experiment, the FRP removal after 24 h was less than predicted by the model.

Several authors have implied that humic substances may have reduced the effectiveness of the LMB Phoslock[®] (Ross et al., 2008; Lüring and Faassen, 2012). Ross et al. (2008) noted that “the presence of humic acids in the water lowered the phosphorus adsorption capacity of Phoslock[®], especially at higher pH values”, but they referred to a confidential CSIRO Report (no. 6/00 2000). Interference with humic substances could correspondingly explain the limited effect of Phoslock[®] in mitigating P release from soils (Geurts et al.,

2011), because rewetting peat can stimulate DOC production (e.g. Cabezas et al., 2013), as well as the limited reduction in water column P concentrations following two Phoslock[®] applications in a 5 ha *claustrum* in The Netherlands (Lüring and Van Oosterhout, 2013a). For the latter and for the enclosure experiment described in Lüring and Faassen (2012), DOC concentrations could be estimated from a relationship between DOC determined by a Shimadzu TOC analyzer and absorbance measurements at 254 nm ($\text{DOC} = 12.80764 \times A_{254}$; $r^2 = 0.999$), yielding 5.3 mg DOC l^{-1} in water of the enclosure-experiment and 5.6 mg DOC l^{-1} in the 5 ha *claustrum*. These values are high enough to expect some interference from humic substances, although other environmental factors, such as naturally occurring oxyanions like carbonates (Johannesson and Lyons, 1994) and pH (Ross et al., 2008) could hinder the effectiveness of LMB as well. As humic substances are known to form complexes with metals (Van Dijk, 1971; Rashid, 1974) in general, our results are consonant to observations that humic substances inhibited the P-removal capacity of alum (Omoike and VanLoon, 1999). Moreover, from this complexation with metals in general, it may be postulated the humic substances can interfere with all other metal-based solids phase phosphate sorbents.

We observed a strong increase of filterable lanthanum in presence of humic substances. The observed values (up to

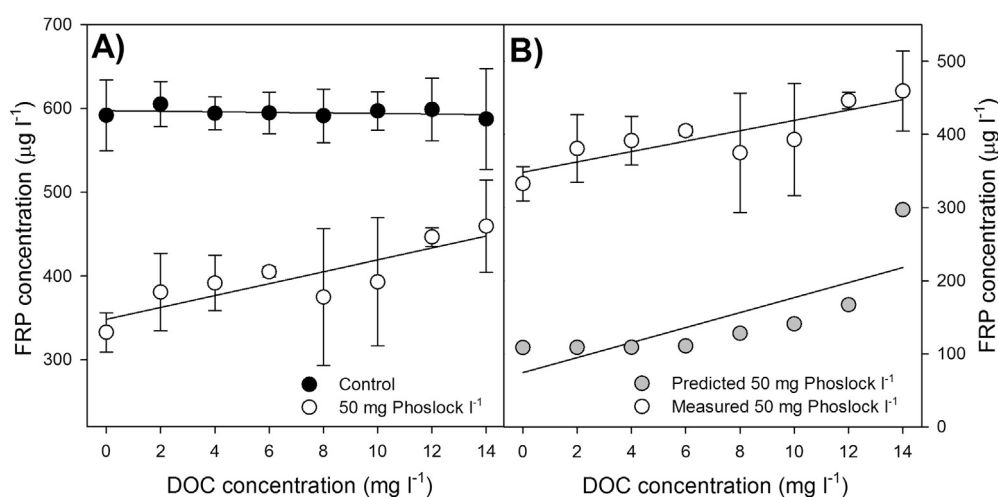


Fig. 2 – Panel A: Filterable reactive phosphorus (FRP) concentrations ($\mu\text{g l}^{-1}$) in water with different humic acid concentrations (0–14 mg DOC l^{-1}) incubated for 24 h in the absence (filled black symbols, control) or presence of 50 mg l^{-1} Phoslock[®]. Panel B: Comparison between measured FRP concentrations (open symbols, $\mu\text{g l}^{-1}$) and those predicted from chemical equilibrium modelling (filled grey symbols) in water with different humic acid concentrations (0–14 mg DOC l^{-1}) incubated for 24 h in the presence of 2182 $\mu\text{g La l}^{-1}$ (from 50 mg l^{-1} Phoslock[®] containing 4.37% La). Error bars indicate 1 SD ($n = 3$), solid lines represent linear regression.

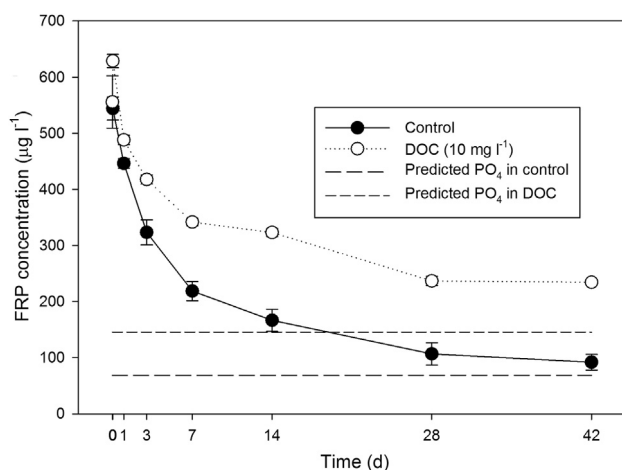


Fig. 3 – Course of the filterable reactive phosphorus (FRP) concentrations ($\mu\text{g l}^{-1}$) in FRP solutions treated with 50 mg l^{-1} Phoslock[®] in absence (control; black symbols) and presence of humic substances (open symbols; 10 mg DOC l^{-1}). Error bars indicate 1 SD ($n = 3$). The medium dashed line represents the predicted residual FRP concentration in controls derived from chemical equilibrium modelling, whereas the short dashed line represents the predicted residual FRP concentration in DOC treatments.

$273 \mu\text{g l}^{-1}$) are in the same range as the monthly mean filterable lanthanum concentrations found in the surface layers of six lakes following upon the application of Phoslock[®] that ranged from $2 \mu\text{g l}^{-1}$ to $414 \mu\text{g l}^{-1}$ (Spears et al., 2013b). However, as the DOC concentrations in most of those waters are not known, we cannot relate the observed difference in that study to DOC. Nonetheless, several studies have shown that humic substances are complexing agent for lanthanides (Sonke and

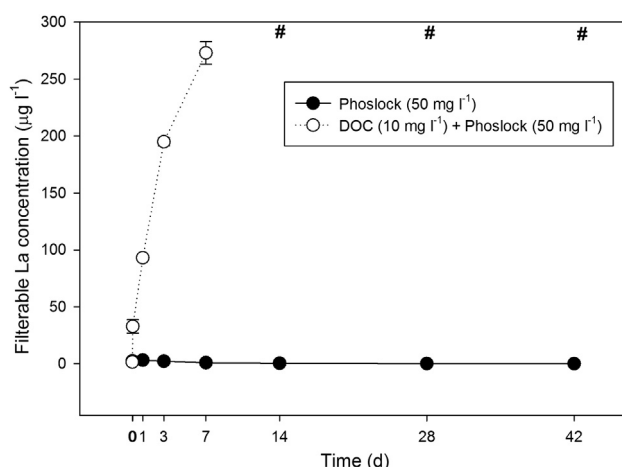


Fig. 4 – Course of the filterable lanthanum (La) concentrations ($\mu\text{g l}^{-1}$) in FRP solutions treated with 50 mg l^{-1} Phoslock[®] in absence (control; black symbols) and presence of humic substances (open symbols; 10 mg DOC l^{-1}). Error bars indicate 1 SD ($n = 3$). # indicates samples that showed precipitation in filtrates.

Salters, 2006; Tang and Johannesson, 2003, 2010a). The presence of humic substances decreased La adsorption onto Carrizo sand through La-humic complex formation (Tang and Johannesson, 2010a). Increased concentrations of Aldrich humic substances increased the amount of La extracted from Carrizo sand (Tang and Johannesson, 2010b). In surface waters, dissolved lanthanides seem primarily associated with humic substances (Tang and Johannesson, 2010b). In a pH range of 6–9 more than 80% of the La is predicted to occur as organic La-humic complexes (Pourret et al., 2007a). Hence, complexation of La with humic substances seems a plausible explanation for the increased filterable La in our experiment (Fig. 5). Dutch legislation allows a maximum filterable La concentration of $10.1 \mu\text{g l}^{-1}$ in surface waters (Sneller et al., 2000). Thus, possible leaching of La from its bentonite matrix is an import issue in the Netherlands. Our current and previous studies (Lüring and Tolman, 2010) contradict the assumption “all La is contained within the clay matrix” (Douglas et al., 2008). In our current and previous studies with Phoslock[®] La was present in $0.45 \mu\text{m}$ filtrate. As the particles in a Phoslock[®] suspension showed a negligible fraction $<0.45 \mu\text{m}$ (Haghseresht, 2005), the passing of Phoslock[®] particles through a $<0.45 \mu\text{m}$ filter does not explain our filtrates. Extraction of La from the bentonite matrix by humic substances seems a probable explanation. Nonetheless, humic substances are also known for complexation of clay minerals (e.g. Tombácz et al., 2004) and despite bentonite-humic substance aggregates may form particles of several micrometres in size (Bilanovic et al., 2007), our study cannot separate La from La-clay colloids (Fig. 5). As the Dutch standard is based on filterable La, the observed strong increase of filterable La in presence of humic substances could imply a serious violation of the Dutch standard and thereby a potential major drawback in application of Phoslock[®] in Dutch DOC-rich water bodies. Here, more long-term experiments with different water types (e.g. varying in DOC, alkalinity, pH) are needed as the filtered lanthanum concentrations after whole lake applications only dropped to below the Dutch standard after several months (Spears et al., 2013b).

Our study and those of others (Moermond et al., 2001; Pourret et al., 2007a; Tang and Johannesson, 2010b) imply that in DOC-rich inland waters the applicability of exclusively Phoslock[®] as FRP binder should be met critically. In natural water, the effectiveness of La to bind FRP is reduced by complexation with humic substances (Pourret et al., 2007b) as well as oxyanions other than FRP (Moermond et al., 2001). Since the action of DOC (Pourret et al., 2007b) and other oxyanions (Moermond et al., 2001) in complexation with La is difficult to predict *a priori* thorough experimental testing of the efficacy of Phoslock[®] in removing FRP in the given water is required prior to application.

In our short term experiment the reduction in the concentration of FRP was less than expected (Fig. 2B). While this experiment was done without agitation, Ferreira and Motta Marques (2009) and Van Oosterhout and Lüring (2013) found comparable results under continuous agitation (50 respectively 200 rpm). In our current study the 24 h FRP removal by the Phoslock[®] (in the absence of DOC) was 46% only, in the study of Ferreira and Motta Marques (2009) it was 63% in 24 h, while Van Oosterhout and Lüring (2013) found a reduction of 68% after 5 h. In these cases the added dose of Phoslock[®] was

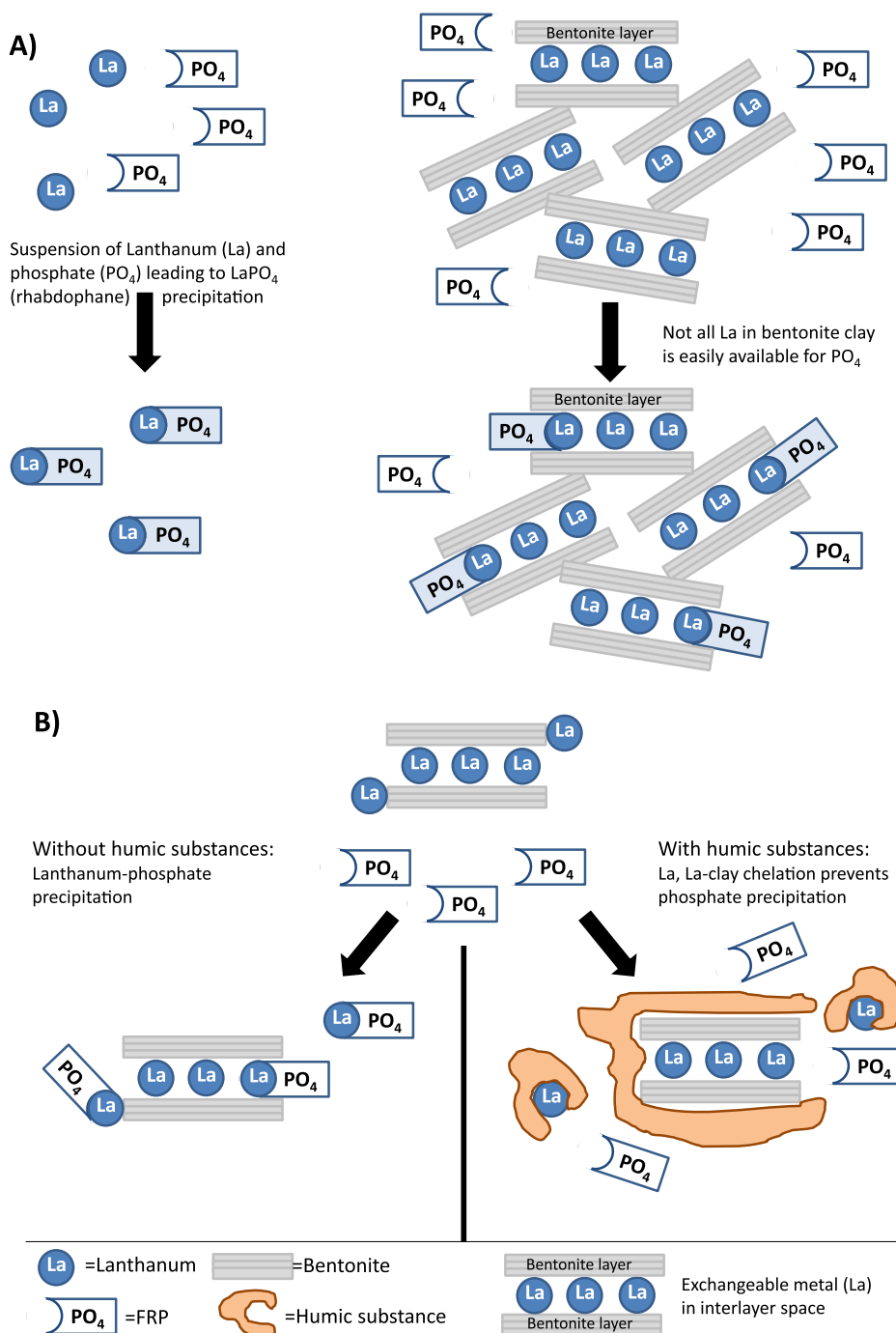


Fig. 5 – Suspension of La and FRP in dissolved phase will lead to precipitation of La-FRP as rhabdophane (panel A, left side), while diffusion of FRP to La in LMB might be hindered (panel A, right side). In absence of humic substances FRP can precipitate with available La binding sites in LMB (panel A, right side; panel B, left side), however humic complexation (chelation) of La and LMB hinders FRP precipitation and may lead to “dissolved” La associated with humic substances (panel B, right side).

theoretically sufficient to bind all FRP, assuming a 1:1 La:phosphate molar ratio (Haghseresht et al., 2009). According to the manufacturer “in most situations, more than 90% of available phosphate is bound within three hours of an application of Phoslock” (<http://www.phoslock.eu/en/phoslock/about-phoslock/> last accessed January 21st 2014). This, however,

could not be confirmed in the present study, where it took 42 days before FRP removal approached the predicted FRP reduction (Fig. 3). In a previous study a dose between 220:1–700:1 was needed to achieve the alleged efficiency under thorough mixing of 200 rpm (Van Oosterhout and Lürling, 2013).

Conversely, Meis et al. (2012) observed a 90% higher FRP binding capacity of Phoslock[®] than its La content would predict – which indicates that Phoslock[®] may have more FRP binding sites. Despite the possible presence of more FRP binding sites in Phoslock[®] our observed FRP removal after 42 days in the absence of DOC (controls) or other oxyanions competing with FRP was still about 34% lower than predicted. While the recommended Phoslock[®]: P dose is 100:1, earlier works of the manufacturer showed that a 100:1 dose reduced FRP only by 50% after 34 h (Haghseresht, 2004) and several subsequent studies used a dose of 230:1 (Haghseresht, 2005; Ross et al., 2008). Moreover, several recent studies showed that advised 100:1 dose appeared insufficient in reducing FRP concentrations to low levels (Reitzel et al., 2013a,b; Van Oosterhout and Lürling, 2013).

One explanation for the delayed FRP sorption by Phoslock[®] may be sought in the structure of Phoslock[®], which is a lanthanum enriched bentonite. Bentonite is an inhomogeneous material composed of clay minerals and grains within which several 'open spaces' exist (Ichikawa et al., 2004). The clay minerals are composed of layers comprising silica and alumina sheets joined together and stacked on top of each other with some interlayer space; the exchangeable cation water layer (Luckham and Rossi, 1999; Ichikawa et al., 2004). Several stacks are packed together forming aggregates with interstitial space, while an assembly of aggregates encloses an inter-aggregate space, a pore with water usually in between macro-grains, such as quartz (Ichikawa et al., 2004; Bergaya and Lagaly, 2006). La will be in the pore water, at external crystal surfaces and probably mostly in the interlayer space (Luckham and Rossi, 1999). The dominating mineral in bentonite is montmorillonite, which has a negatively charged surface that will affect the behaviour of anions like FRP within its structure (Molera et al., 2003). Consequently, the rate of FRP absorption in clay suspension will be lower compared to a solution of free La as phosphates need to diffuse to all active sites (Fig. 5). This low absorption rate is evident from our long-term experiment, where after 6 weeks residual FRP concentrations were still on average 34% higher than predicted. Hence, in addition to presence of humic substances also contact time (and mixing) of Phoslock[®] particles in the water column seem important in FRP-removal efficiency as was evident from comparison of our short term experiment with other short term experiments under continuous agitation (50 rpm; Ferreira and Motta Marques, 2009; 200 rpm; Van Oosterhout and Lürling, 2013). In still water Phoslock[®] particles showed rapid settling out of the water column (Van Oosterhout and Lürling, 2013). Application under windy conditions might prolong contact time of Phoslock[®] particles in the water column, but could also lead to inhomogeneous distribution due to water currents transporting suspended matter (Van Duin et al., 2001), meanwhile there is no reason to expect that prolonged mixing will mitigate the inhibiting effect of humic substances.

The aim of our experiments was to show the effects of humic substances on the P binding capacity by the LMB. Hence, we aimed at lifting this hypothesized effect well out of possible variances to be expected in the experiments. In our experiments we used FRP concentrations of 600 µg l⁻¹ that are

relatively high as compared to field concentrations mostly observed. However – under anoxia, hypolimnion FRP concentrations or summer FRP can be elevated to concentrations as high or higher than the ones we have used (e.g. Reitzel et al., 2005). Inasmuch as the prime target of the LMB is to reduce sediment P release, we consider the high FRP concentrations used as realistic. Nonetheless, further experiments could include a range of FRP concentrations and corresponding LMB doses.

Flocculants like polyaluminiumchloride (PAC) can remove humic substances from the water column (Kuo and Amy, 1988; Yan et al., 2008; Liu et al., 2009). The application of PAC has the additional advantage of reducing suspended particulate matter (Jekel, 1986), i.e. during a water bloom of cyanobacteria most water column P is particulate and thus outside the mode of action of Phoslock[®]. PAC has additional advantage (over other flocculants) that it also binds FRP (Lopata and Gawronska, 2008). Our previous experiments have shown that the La modified clay does not effectively remove cyanobacteria from the water column – i.e. the clay does not flocculate in freshwater, but in combination with PAC cyanobacteria are effectively removed (Lürling and Van Oosterhout, 2013b). The combination of a flocculent and Phoslock[®] was applied to Lake Rauwbraken in April 2008 (Lürling and Van Oosterhout, 2013b), where it resulted in strong reduced water column TP concentrations that has lasted until present – thus for at least more than six growing seasons (five years). Using absorption at 380 nm (A_{380}) as a proxy for humic substances, we could show that humic substances concentration in Lake Rauwbraken was reduced from $A_{380} = 2.0 \text{ m}^{-1}$ before (range 1.0–7.3 m^{-1}) to $A_{380} = 0.6 \text{ m}^{-1}$ (range 0.5–0.7 m^{-1}) after treatment (Lürling and Van Oosterhout, 2013b). Therefore, combination of a flocculent and LMB can be advised above a sole LMB treatment in humic rich water bodies and/or waters with already a cyanobacterial bloom present, for which additional experiments would make a logical follow-up of this study.

Our results show that variability among lakes in both chemical composition of waters and sediments is one of the most important differences between lakes that may influence the effectiveness of chemical P inactivation. More specific, humic substances may play a far more important role in the success or failure of chemical P inactivation than thus far appreciated.

Humic substances are present in eutrophic/dystrophic waters generally in concentrations similar or exceeding the ones employed in our study (Thurman, 1985). In The Netherlands for example De Lange (2000) reported a median DOC concentration of 9.8 mg l⁻¹ from 19 surface waters, while in the period January 1st 2008 until November 5th 2013, the median DOC concentration of all surface water measurements in the jurisdiction of the RWA Brabantse Delta was 10.9 mg l⁻¹ ($n = 1849$). Climate change is predicted to increase leakage of terrestrial humic substances to surface waters (Monteith et al., 2007; Ekvall et al., 2013). Hence, humic substances are already expected to play a substantial role in lowering the efficacy of metal-based FRP-sorbents and this is expected to increase in future, which makes measurements of humic substances (DOC) as well as controlled experiments vital.

5. Conclusions

Based on the results of this study it can be concluded that

- Humic substances interfere with FRP-removal of the La-modified bentonite Phoslock®.
- The concentration of filterable La strongly increased in presence of humic substances.
- The contact time of Phoslock® particles in the water column is important in FRP-removal efficacy.
- The recommended dose of Phoslock® seems too low.
- Thorough experimental testing of the efficacy of Phoslock® in removing FRP in a given water is required prior to application.

Acknowledgements

This study was sponsored by a Water Framework Directive Innovation Grant of AgentschapNL of the Ministry of Economic Affairs and by a subsidy of the Province of Noord-Brabant. We thank Irene Paredes, Valentini Maliaka and Wendy Beekman for assistance with the experiments.

REFERENCES

- Akhurst, D., Jones, G.B., McConchie, D.M., 2004. The application of sediment capping agents on phosphorus speciation and mobility in a sub-tropical Dunal lake. *Mar. Freshw. Res.* 55, 715–725.
- Bergaya, F., Lagaly, G., 2006. General introduction: clays, clay minerals and clay science. In: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), *Handbook of Clay Science*. Elsevier, pp. 1–18.
- Bilanovic, D.D., Kroeger, T.J., Spigarelli, S.A., 2007. Behaviour of humic-bentonite aggregates in diluted suspensions. *Water SA* 33 (1), 111–116.
- Cabezas, A., Gelbrecht, J., Zak, D., 2013. The effect of rewetting drained fens with nitrate-polluted water on dissolved organic carbon and phosphorus release. *Ecol. Eng.* 53, 79–88.
- Codd, G.A., Morrison, L.F., Metcalf, J.S., 2005. Cyanobacterial toxins: risk management for health protection. *Toxicol. Appl. Pharmacol.* 203 (3), 264–272.
- Conley, D.J., Paerl, H.W., Howarth, R.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009. Controlling eutrophication by reducing both nitrogen and phosphorus. *Science* 323, 1014–1015.
- Cooke, G.D., Welch, E.B., Martin, A.B., Fulmer, D.G., Hyde, J.B., Schreive, G.D., 1993. Effectiveness of Al, Ca and Fe salts for control of internal P loading in shallow and deep lakes. *Hydrobiologia* 253, 323–335.
- Cooke, G.D., Welch, E.B., Peterson, S.A., Nichols, S.A., 2005. *Restoration and Management of Lakes and Reservoirs*, third ed. CRC Press, Taylor & Francis Group, Boca Raton, USA.
- De Lange, H.J., 2000. The attenuation of ultraviolet and visible radiation in Dutch inland waters. *Aquat. Ecol.* 34, 215–226.
- Dittmann, E., Wiegand, C., 2006. Cyanobacterial toxins – occurrence, biosynthesis and impact on human affairs. *Mol. Nutr. Food Res.* 50 (1), 7–17.
- Douglas, G.B., 2002. US Patent 6350383: Remediation Material and Remediation Process for Sediments.
- Douglas, G.B., Robb, M.S., Coad, D.N., Ford, P.W., 2004. A review of solid phase adsorbents for the removal of phosphorus from natural and waste waters. In: Valsami-Jones, E. (Ed.), *Phosphorus in Environmental Technology – Removal, Recovery, Applications*. IWA Publishing, pp. 291–320 (Chapter 13).
- Douglas, G.B., Robb, M.S., Ford, P.W., 2008. Reassessment of the performance of mineral- based sediment capping materials to bind phosphorus: a comment on Akhurst (2004). *Mar. Freshw. Res.* 59, 836–837.
- Ekvall, M.K., De La Calle Martin, J., Faassen, E.J., Gustafsson, S., Lüring, M., Hansson, L.-A., 2013. Synergistic and species-specific effects of climate change and water colour on cyanobacterial toxicity and bloom formation. *Freshw. Biol.* 58, 2414–2422.
- European Union, 2000. Directive 2000/60/EG of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy of 23 October. PB L 327 of 22 December 2000.
- Finkler Ferreira, T., Da Motta Marques, D.M.L., 2009. The use of Phoslock® to remove phosphorous and control toxic cyanobacteria. *Rev. Bras. Recur. Hídricos* 14, 73–82.
- Geurts, J.J.M., van de Wouw, P.A.G., Smolders, A.J.P., Roelofs, J.G.M., Lamers, L.P.M., 2011. Ecological restoration on former agricultural soils: feasibility of in situ phosphate fixation as an alternative to top soil removal. *Ecol. Eng.* 37 (11), 1620–1629.
- Gibbs, M.M., Hickey, C.W., Özkundakci, D., 2011. Sustainability assessment and comparison of efficacy of four P-inactivation agents for managing internal phosphorus loads in lakes: sediment incubations. *Hydrobiologia* 658, 253–275.
- Haghseresht, F., 2004. The Use of Phoslock™ in Reducing Filterable Reactive Phosphorous Level in Water Bodies: an Overview of the Properties of Phoslock™ and its Performance in Improving Water Quality. Integrated Mineral Technology Pty Ltd. Report.
- Haghseresht, F., 2005. A Revolution in Phosphorous Removal. Phoslock Water Solutions Ltd., p. 21. <http://www.phoslock.com.au>
- Haghseresht, F., Wang, S., Do, D.D., 2009. A novel lanthanum-modified bentonite, Phoslock, for phosphate removal from wastewaters. *Appl. Clay Sci.* 46 (4), 369–375.
- Ichikawa, Y., Kawamura, K., Fujii, N., Kitayama, K., 2004. Microstructure and micro/macro-diffusion behavior of tritium in bentonite. *Appl. Clay Sci.* 26, 75–90.
- Jekel, M.R., 1986. Interactions of humic acids and aluminum salts in the flocculation process. *Water Res.* 20 (12), 1535–1542.
- Johannesson, K.H., Lyons, W.B., 1994. The rare earth element geochemistry of Mono Lake water and the importance of carbonate complexing. *Limnol. Oceanogr.* 39, 1141–1154.
- Klapper, H., 2003. Technologies for lake restoration. *J. Limnol.* 62 (Suppl. 1), 73–90.
- Kuo, C.-J., Amy, G.L., 1988. Factors affecting coagulation with aluminum sulfate-II. Dissolved organic matter removal. *Water Res.* 22 (7), 863–872.
- Liu, X., Byrne, R.H., 1997. Rare earth and yttrium phosphate solubilities in aqueous solution. *Geochim. Cosmochim. Acta* 61 (8), 1625–1633.
- Liu, H., Hu, C., Zhao, H., Qu, J., 2009. Coagulation of humic acid by PACl with high content of Al₁₃: the role of aluminum speciation. *Sep. Purif. Technol.* 70 (2), 225–230.
- Lopata, M., Gawrońska, H., 2008. Phosphorus immobilization in Lake Głęboczek following treatment with polyaluminum chloride. *Oceanol. Hydrobiolog. Stud.* 37 (2), 99–105.
- Luckham, P.F., Rossi, S., 1999. The colloidal and rheological properties of bentonite suspensions. *Adv. Colloid Interface Sci.* 82, 43–92.
- Lüring, M., Faassen, E.J., 2012. Controlling toxic cyanobacteria: effects of dredging and phosphorus-binding clay on cyanobacteria and microcystins. *Water Res.* 46 (5), 1447–1459.

- Lürling, M., Tolman, Y., 2010. Effects of lanthanum and lanthanum-modified clay on growth, survival and reproduction of *Daphnia magna*. *Water Res.* 44 (1), 309–319.
- Lürling, M., Van Oosterhout, F., 2013a. Case study on the efficacy of a lanthanum-enriched clay (Phoslock®) in controlling eutrophication in Lake Het Groene Eiland (The Netherlands). *Hydrobiologia* 710 (1), 253–263.
- Lürling, M., Van Oosterhout, F., 2013b. Controlling eutrophication by combined bloom precipitation and sediment phosphorus inactivation. *Water Res.* 47 (17), 6527–6537.
- Mehner, T., Diekmann, M., Gonsiorczyk, T., Kasprzak, P., Koschel, R., Krienitz, L., Rumpf, M., Schulz, M., Wauer, G., 2008. Rapid recovery from eutrophication of a stratified lake by disruption of internal nutrient load. *Ecosystems* 11, 1142–1156.
- Meis, S., Spears, B.M., Maberly, S.C., O'Malley, M.B., Perkins, R.G., 2012. Sediment amendment with Phoslock in Clatto Reservoir (Dundee, UK): investigating changes in sediment elemental composition and phosphorus fractionation. *J. Environ. Manage.* 93, 185–193.
- Moermond, C.T.A., Tijnk, J., van Wezel, A.P., Koelmans, A.A., 2001. Distribution, speciation, and bioavailability of lanthanides in the Rhine-Meuse estuary, The Netherlands. *Environ. Toxicol. Chem.* 20 (9), 1916–1926.
- Molera, M., Eriksen, T., Jansson, M., 2003. Anion diffusion pathways in bentonite clay compacted to different dry densities. *Appl. Clay Sci.* 23, 69–76.
- Monteith, D.T., Stoddard, J.L., Evans, C.D., De Wit, H.A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B.L., Jeffries, D.S., Vuorenmaa, J., Keller, B., Kopáček, J., Vesely, J., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450, 537–541.
- NNI, 1986. Water: Photometric Determination of the Content of Dissolved Orthophosphate and the Total Content of Phosphorous Compounds by Continuous Flow Analysis. Netherlands Normalization Institute, Delft, The Netherlands. NEN 6663.
- Omoike, A.I., Vanloon, G.W., 1999. Removal of phosphorus and organic matter removal by alum during wastewater treatment. *Water Res.* 33 (17), 3617–3627.
- Paerl, H.W., 2009. Controlling eutrophication along the freshwater–marine continuum: dual nutrient (N and P) reductions are essential. *Estuar. Coast.* 32 (4), 593–601.
- Pourret, O., Davranche, M., Gruau, G., Dia, A., 2007a. Rare earth elements complexation with humic acid. *Chem. Geol.* 243 (1–2), 128–141.
- Pourret, O., Davranche, M., Gruau, G., Dia, A., 2007b. Organic complexation of rare earth elements in natural waters: evaluating model calculations from ultrafiltration data. *Geochim. Cosmochim. Acta* 71 (11), 2718–2735.
- Rashid, M.A., 1974. Absorption of metals on sedimentary and peat humic acids. *Chem. Geol.* 13 (2), 115–123.
- Reitzel, K., Hansen, J., Andersen, F.Ø., Hansen, K., Jensen, H.S., 2005. Lake restoration by dosing aluminum relative to mobile phosphorus in the sediment. *Environ. Sci. Technol.* 39 (11), 4134–4140.
- Reitzel, K., Andersen, F.Ø., Egemose, S., Jensen, H.S., 2013a. Phosphate adsorption by lanthanum modified bentonite clay in fresh and brackish water. *Water Res.* 47 (8), 2787–2796.
- Reitzel, K., Lotter, S., Dubke, M., Egemose, S., Jensen, H.S., Andersen, F.Ø., 2013b. Effects of Phoslock® treatment and chironomids on the exchange of nutrients between sediment and water. *Hydrobiologia* 703, 189–202.
- Robb, M., Greenop, B., Goss, Z., Douglas, G., Adeney, J., 2003. Application of Phoslock™, an innovative phosphorus binding clay, to two Western Australian waterways: preliminary findings. *Hydrobiologia* 494, 237–243.
- Ross, G., Haghseresht, F., Cloete, T.M., 2008. The effect of pH and anoxia on the performance of Phoslock®, a phosphorus binding clay. *Harmful Algae* 7, 545–550.
- Schindler, D.W., Hecky, R.E., Findlay, D.L., Stainton, M.P., Parker, B.R., Paterson, M.J., Beaty, K.G., Lyng, M., Kasian, S.E.M., 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. *Proc. Natl. Acad. Sci. U S A* 105 (32), 11254–11258.
- Smith, V.H., Schindler, D.W., 2009. Eutrophication science: where do we go from here? *Trends Ecol. Evol.* 24, 201–207.
- Smith, V.H., Tilman, G.D., Nekola, J.C., 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environ. Pollut.* 100 (1–3), 179–196.
- Sonke, J.E., 2006. Lanthanide-Humic substances complexation. II. Calibration of humic ion-binding model V. *Environ. Sci. Technol.* 40, 7481–7487.
- Sonke, J.E., Salters, V.J.M., 2006. Lanthanide–humic substances complexation. I. Experimental evidence for a lanthanide contraction effect. *Geochim. Cosmochim. Acta* 70 (6), 1495–1506.
- Spears, B.M., Meis, S., Anderson, A., Kellou, M., 2013a. Comparison of phosphorus (P) removal properties of materials proposed for the control of sediment P release in UK lakes. *Sci. Total Environ.* 442, 103–110.
- Spears, B.M., Lürling, M., Yasseri, S., Castro-Castellon, A.T., Gibbs, M., Meis, S., McDonald, C., Castro-Castellon, A., Gibbs, M., 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 (15), 5930–5942.
- Sneller, F.E.C., Kalf, D.F., Weltje, L., van Wezel, A.P., 2000. Maximum Permissible Concentrations and Negligible Concentrations for Rare Earth Elements (REEs). RIVM report 601501011.
- Tang, J., Johannesson, K.H., 2003. Speciation of rare earth elements in natural terrestrial waters: assessing the role of dissolved organic matter from the modeling approach. *Geochim. Cosmochim. Acta* 67 (13), 2321–2339.
- Tang, J., Johannesson, K.H., 2010a. Ligand extraction of rare earth elements from aquifer sediments: implications for rare earth element complexation with organic matter in natural waters. *Geochim. Cosmochim. Acta* 74 (23), 6690–6705.
- Tang, J., Johannesson, K.H., 2010b. Rare earth elements adsorption onto Carrizo sand: influence of strong solution complexation. *Chem. Geol.* 279, 120–133.
- Thurman, E.M., 1985. Amount of organic carbon in natural waters. In: Thurman, E.M. (Ed.), *Organic Geochemistry of Natural Waters, Developments in Biogeochemistry*, vol. 2. Nijhoff & Junk Publ., Boston, pp. 7–65.
- Tipping, E., 1994. WHAMC-A chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Comput. Geosci.* 20 (6), 973–1023.
- Tipping, E., Hurley, M.A., 1992. A unifying model of cation binding by humic substances. *Geochim. Cosmochim. Acta* 56 (10), 3627–3641.
- Tombácz, E., Libor, Z., Illés, Z., Majzik, A., Klumpp, E., 2004. The role of reactive surface sites and complexation by humic acids in the interaction of clay mineral and iron oxide particles. *Org. Geochem.* 35, 257–267.
- Van Dijk, H., 1971. Cation binding of humic acids. *Geoderma* 5 (1), 53–67.
- Van Duin, E.H.S., Blom, G., Los, F.J., Maffione, R., Zimmerman, R., Cerco, C.F., Dortch, M., Best, E.P.H., 2001. Modeling underwater light climate in relation to sedimentation, resuspension, water quality and autotrophic growth. *Hydrobiologia* 444, 25–42.
- Van Oosterhout, F., Lürling, M., 2013. The effect of phosphorus binding clay (Phoslock®) in mitigating cyanobacterial nuisance: a laboratory study on the effects on water quality variables and plankton. *Hydrobiologia* 710, 265–277.
- Verweij, W., 2013. CHEAQS, a Program for Calculating CHEMical Equilibria in AQUatic Systems, PRO Version (2013.1).

- Yan, M., Wang, D., Nia, J., Qu, J., Chow, C.W.K., Liu, H., 2008. Mechanism of natural organic matter removal by polyaluminum chloride: effect of coagulant particle size and hydrolysis kinetics. *Water Res.* 42 (13), 3361–3370.
- Yang, S.-Q., Liu, P.-W., 2010. Strategy of water pollution prevention in Taihu Lake and its effects analysis. *J. Gt. Lakes. Res.* 36 (1), 150–158.
- Yuan, X.-Z., Pan, G., Chen, H., Tian, B.-H., 2009. Phosphorus fixation in lake sediments using LaCl_3 -modified clays. *Ecol. Eng.* 35 (11), 1599–1602.
- Zamparas, M., Gianni, A., Stathi, P., Deligiannakis, Y., Zacharias, I., 2012. Removal of phosphate from natural waters using innovative modified bentonites. *Appl. Clay Sci.* 62–63, 101–106.