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SHALLOW LAKE ECOSYSTEMS

Case study on the efficacy of a lanthanum-enriched clay (Phoslock®) in controlling eutrophication in Lake Het Groene Eiland (The Netherlands)

Miquel Lürling · Frank van Oosterhout

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Abstract Lake Het Groene Eiland was created in the beginning of 2008 by construction of dikes for isolating it from the surrounding 220-ha water body. This so-called *claustrum* of 5 ha was treated using lanthanum-modified clay (Phoslock®) to control eutrophication and mitigate cyanobacterial nuisance. Cyanobacteria chlorophyll-*a* were significantly lower in the *claustrum* than those in the reference water body, where a massive bloom developed in summer, 2008. However, PO_4-P and TP did not statistically differ in these two waters. TN and NO_3-N were significantly lower in the *claustrum*, where dense submerged macrophytes beds developed. Lanthanum concentrations were elevated after the applications of the modified clay in the *claustrum*, but filterable lanthanum dropped rapidly below the Dutch standard of 10.1 $\mu g\ l^{-1}$. During winter, dozens of Canada geese resided at the *claustrum*. Geese droppings contained an average of 2 mg PO_4-P g^{-1} dry weight and 12 mg NH_3-N g^{-1} dry weight and might present a growing source of nutrients to the water. Constructing the *claustrum* enabled unrestricted bathing in subsequent three summers, as no swimming bans had to be issued due to cyanobacteria blooms. However, the role of the modified clay in this positive outcome remains unclear, and longevity of the measures questionable.

Keywords Algal blooms · Cyanobacteria · Phosphorus fixation · Lake restoration · Mitigation measures

Introduction

Eutrophication is identified as a major water quality management issue for lakes and rivers in the Netherlands (Roijackers et al., 1998) as in the case of many freshwater systems worldwide (Smith & Schindler, 2009). A prime symptom of eutrophication is massive cyanobacterial blooms that pose a serious environmental problem and risk to human health. Blooms may cause high turbidity, anoxia, fish kills, and produce food web alterations causing foul odors, and they may contain various potent toxins (Codd et al., 2005; Dittmann & Wiegand, 2006; Paerl, 2008; Paerl & Huisman, 2008, 2009). The incidence and intensity of such blooms are expected to increase in future because of climate

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M. Lürling (✉) · F. van Oosterhout
Aquatic Ecology & Water Quality Management Group,
Department of Environmental Sciences, Wageningen
University, P.O. Box 47, 6700 AA Wageningen,
The Netherlands
e-mail: miquel.lurling@wur.nl

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

changes and the increasing world's human population (Paerl & Huisman, 2008, 2009).

Controlling eutrophication and mitigating nuisance are key challenges to water quality managers and pose as important problems confronting the European Water Framework Directive (EU, 2000) and the EU Bathing Water Directive (EU, 2006). In the Netherlands, many lake restoration attempts in the past had been reported to have failed because of inadequate actions against the phosphorous (P) inputs from both external sources and from the P-rich, often anoxic, lake sediments (Gulati & Van Donk, 2002). These sediments became fully loaded with P because of uncontrolled external P inputs for decades. Hence, mitigating eutrophication requires P control (Carpenter, 2008; Schindler et al., 2008) from input waters as well as the internal loading from the sediment (Carpenter et al., 1998; Søndergaard et al., 2003; Welch & Cooke, 2005; Mehner et al., 2008). The lanthanum-modified clay water treatment technology (Phoslock®) that was developed by CSIRO Australia (Douglas, 2002) seems quite promising in intercepting P released from the P-rich bottom sediments (Robb et al., 2003; Akhurst et al., 2004; Douglas et al., 2004; Ross et al., 2008) and thus could provide a welcome alternative to removal of P-rich sediments.

In the Netherlands (April 2008), Phoslock® was first applied in a 5-ha water body that had been isolated from the surrounding 220-ha water body by construction of dikes, which is the subject of this study. This enclosed *claustrum* was named Lake Het Groene Eiland and was created to prevent inflow of water carrying cyanobacteria scums from the surrounding main water body, while the Phoslock® was added to both reduce the P in the water and block P release from the sediment to prevent cyanobacteria proliferation in the *claustrum*.

Although several laboratory studies underpin the potential of Phoslock® in fixing P (e.g., Douglas et al., 1999, 2004; Akhurst et al., 2004; Ross et al., 2008; Finkler Ferreira & Da Motta Marques, 2009; Haghseresht et al., 2009; Van Oosterhout & Lürling, this volume), and at least 11 lakes in Europe have been thus treated since 2006,[1] there are hardly any published scientific papers. Van Oosterhout & Lürling (2011) presented some results of a combined treatment of Phoslock® with the flocculent polyaluminiumchloride in Lake Rauwbraken (The Netherlands). Very recently, Meis et al. (2012) reported on sediment P characteristics in Lake Clatto (Scotland) during a 28-day post-application sampling period from the lake. Van Oosterhout & Lürling (2011) reported on a Flock & Lock treatment in a deep lake describing the water quality variables starting from 10 days before and ending on 18th day after the application. However, promising as the Phoslock® technology may seem, its effectiveness is closely related to the longevity of the treatment in lowering P. Therefore, we monitored both the treated Lake Het Groene Eiland and the untreated surrounding lake for a period of over 28 months. Based on the strong binding of phosphate with the lanthanum in Phoslock® (see Van Oosterhout & Lürling, this volume), we expected that both PO_4-P and TP would be significantly lower in the treated *claustrum* than in the untreated surrounding lake and consequently that cyanobacteria would be virtually absent from the *claustrum*, but not from the surrounding lake. Despite several studies having reported Phoslock® to be promising in controlling eutrophication, our case study shows it does not always live up to this expectation. We discuss why the role of Phoslock® in mitigating eutrophication in this case remains unclear.

Materials and methods

Site description

Het Groene Eiland (51°50′02.39″N, 5°32′55.53″E) is part of a 220-ha lake area called De Gouden Ham that originated in a former meander of the river Maas as a result of sand excavation during the 1970s (Fig. 1). The lake is located between the villages Maasbommel and Appeltern near the city of Nijmegen, and it has a connection with the river Maas. Nowadays, the lake area is used for recreation. However, regular cyanobacterial blooms until 2007 had led to frequent closure of the area to recreation. In 2005, the Recreation Corporation launched a series of measures with the aim to eradicate the cyanobacteria nuisance. The use of pumps, oil screens, and ultrasound devices turned out to be completely ineffective in controlling cyanobacteria outbreaks and nuisance (Kardinaal et al., 2008).

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[1] http://www.phoslock.eu/?subject=en-case-studies.

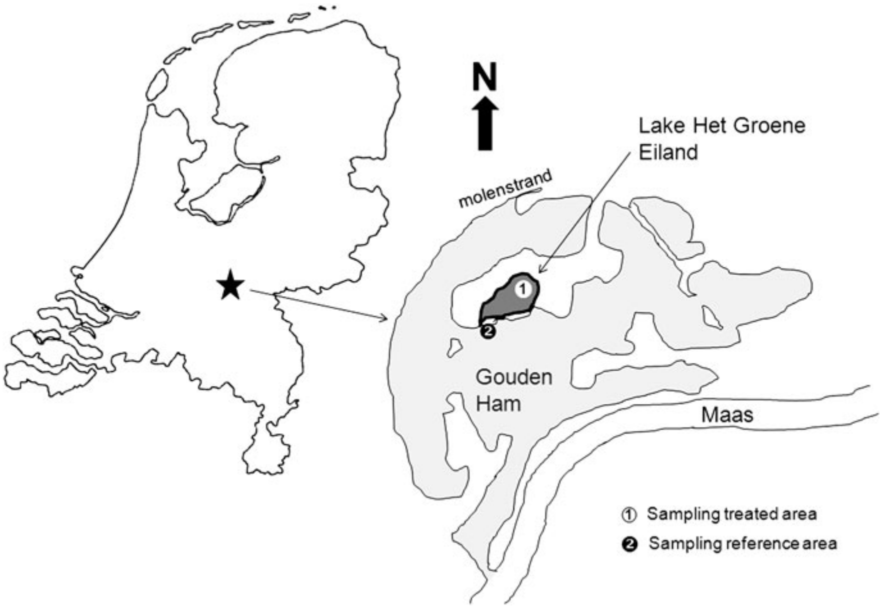

Fig. 1 Location of Lake Het Groene Eiland in the Netherlands (indicated by the *star*: 51°50′02.39″N, 5°32′55.53″E), a schematic drawing of the lake (*dark gray*) in the 220-ha Gouden Ham water system (*light gray*) near the river Maas and the sampling sites in both the enclosed Phoslock®-treated lake (①) and the surrounding reference (❷)

In winter 2008, the three dikes were constructed to isolate the swimming area Het Groene Eiland from the surrounding water body, De Gouden Ham (Fig. 1). The formation of this *claustrum* (meaning “enclosure,” derived from Latin verb *claudere*, i.e., to close) enabled management of the water quality at this bathing site independently from the De Gouden Ham. The *claustrum* has a surface area of ca. 5 ha, a maximum depth of 4.5 m, a mean depth of 2.5 m, and water volume of 130,000 m^3. The main sources of water input to the lake are through precipitation and ground water; the *claustrum* has no outflow. The lake’s bottom sediment was sampled with an Ekman-Birge sampler down to ca. 10-cm sediment depth. The sediment was mostly sandy–clayish, and it contained >1.5 g P kg^{-1} dry weight of the sediment, of which about 0.4 g P kg^{-1} was potential releasable P, which is the sum of immediate releasable P (loosely bound and pore water P), redox-sensitive P (mainly bound to Fe and Mn) and P in micro-organisms, detritus, and humus.[2]

In addition to the formation of the *claustrum,* overhanging vegetation (several trees) was removed and a reed bed of about 2,000 items (*Phragmites australis*) was planted with the intention of harvesting reed every 2 years and thereby removing nutrients.[3]

Phoslock® application

The Phoslock® dose estimation and the application in Lake Het Groene Eiland were performed by the Germany-based companies, Bentophos GmbH and Phoslock® Europe GmbH. On October 15 and December 13, 2007, sediment samples were taken and subjected to sequential sediment P fractionation to determine potential releasable P (Hupfer et al., 1995). The recommended dosage ratio of 100 g Phoslock® to 1 g of phosphate (Afsar & Groves, 2009), the dose of the modified clay (Phoslock®) was based on estimates of the potential releasable phosphorus pool in water and sediment, which was estimated to be 110 kg for the entire *claustrum.*[4] On April 16 and 17, 2008, 11 tons of Phoslock® was applied to the 5-ha site as a slurry that was dispersed onto the lake from a spray

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[2] http://static.phoslock.eu/Upload/pdf-documents/Interim_Report_Het_Groene_Eiland_November_08.pdf.

[3] http://www.blauwalgen.eu/English/Onderzoek.htm.

[4] http://static.phoslock.eu/Upload/pdf-documents/Interim_Report_Het_Groene_Eiland_November_08.pdf, http://www.phoslock.eu/?subject=en-Het-Groene-Eiland, http://static.phoslock.eu/Upload/pdf-documents/Portfolio_HGE.pdf.

boom mounted on the back of a barge. This application of Phoslock® targeted the phosphorus from the available nutrient pool of both the water column and the releasable fraction of the sediment[5]; a second application of 3.1 tons of Phoslock® was done on March 31, 2009 to counteract 31 kg P input from groundwater and (unintentional) run-off from nutrient-rich ash that originated from a large wood fire on one of the banks.[6] The first Phoslock® application lowered the potentially releasable P fraction in the sediment, from 27.2% of the total sediment P (423 mg kg^{-1}) just before the application on April 16, 2008 to 24.1% (352 mg kg^{-1}) after the application on May 22, 2008.[7]

Water quality monitoring

From the start of the Phoslock® application (April 16, 2008) to the end (August 25, 2010), water quality variables were determined regularly in the both enclosed swimming area Het Groene Eiland (treatment; ① in Fig. 1) and the surrounding De Gouden Ham lake area (reference; ❷ in Fig. 1). There was one sampling point in each of the water bodies (Fig. 1). Water temperature (°C), oxygen concentration (mg l^{-1}), pH, and electric conductivity (EC, µS cm^{-1}) were measured using a WTW-350i meter. Water samples collected with a Uwitech water sampler were transferred to the laboratory and further analyzed. Chlorophyll-*a* concentrations were measured using a PHYTO-PAM phytoplankton analyzer (Heinz Walz GmbH, Effeltrich, Germany). The turbidity was measured using a HACH 2100P turbidity meter. The PHYTO-PAM phytoplankton analyzer uses four different excitation wavelengths, which allow separating cyanobacteria, green algae, and diatoms quantitatively (Heinz Walz GmbH, 1999; Lürling & Roessink, 2006). For determining dissolved nutrients and lanthanum (the active ingredient in Phoslock®), water samples were filtered through Whatman GF-C filters. NH_3-N, NO_2/NO_3-N, and PO_4-P and total nutrients (TN and TP) were determined using a Skalar continuous flow analyzer according to the Dutch standard protocols (NNI, 1986, 1990, 1997). Dissolved and total lanthanum (La) was measured by ICP-MS in the Chemical–Biological Soil Laboratory of the Department of Soil Sciences (Wageningen University). The detection limits for La were 0.02 and 0.2 µg l^{-1} for dissolved and total La, respectively. The number of birds on the shore and immediate surroundings of the lake was recorded, and droppings along the shore line were collected for nutrient analysis. The water was visually inspected for the presence of surface scums. All the water quality variables were statistically analyzed by repeated measures analysis of variance in the tool pack SigmaPlot for Windows version 11.0. Slopes of linear regressions of the EC in the *claustrum* and the reference were statistically compared using GraphPad Prism version 5.04.

Results

After formation of the *claustrum*, cyanobacterial blooms and scums appeared no longer at this site, while at the reference site in the surrounding lake, a swimming ban was issued in August–September 2008. At the northern beach of the surrounding water body (location Molenstrand; Fig. 1), a surface scum that had accumulated comprised *Microcystis aeruginosa*, *M. wesenbergii* and some *Pseudoanabaena* sp. with a chlorophyll-*a* concentration of 73 mg l^{-1}. Also at the reference sampling location in the surrounding lake, concentrations of cyanobacteria- and total chlorophyll-*a* were much higher during that period than those in the *claustrum* (Fig. 2). In 2008, the annual mean (±1 SD) cyanobacteria chlorophyll-*a* concentration at the reference site was 21.1 (±34.8) µg l^{-1}, while it was only 1.2 (±2.4) µg l^{-1} in the *claustrum*. In the next year, 2009, mean (±1 SD) cyanobacteria chlorophyll-*a* concentrations were 0.9 (±6.0) and 0.2 (±0.3) in the reference and the *claustrum*, respectively, whereas in 2010, they were 1.4 (±1.8) and 0.2 (±0.2), respectively (Fig. 2). Hence, cyanobacteria chlorophyll-*a* concentrations were lower in the *claustrum* than those in the surrounding lake, which is also reflected in the average cyanobacteria chlorophyll-*a* concentration value (±1 SD) over the entire monitoring period, which was 0.5 (±1.5) in the

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[5] http://static.phoslock.eu/Upload/pdf-documents/Interim_Report_Het_Groene_Eiland_November_08.pdf, http://static.phoslock.eu/Upload/pdf-documents/Portfolio_HGE.pdf.

[6] http://static.phoslock.eu/Upload/pdf-documents/Portfolio_HGE.pdf.

[7] http://static.phoslock.eu/Upload/pdf-documents/Interim_Report_Het_Groene_Eiland_November_08.pdf.

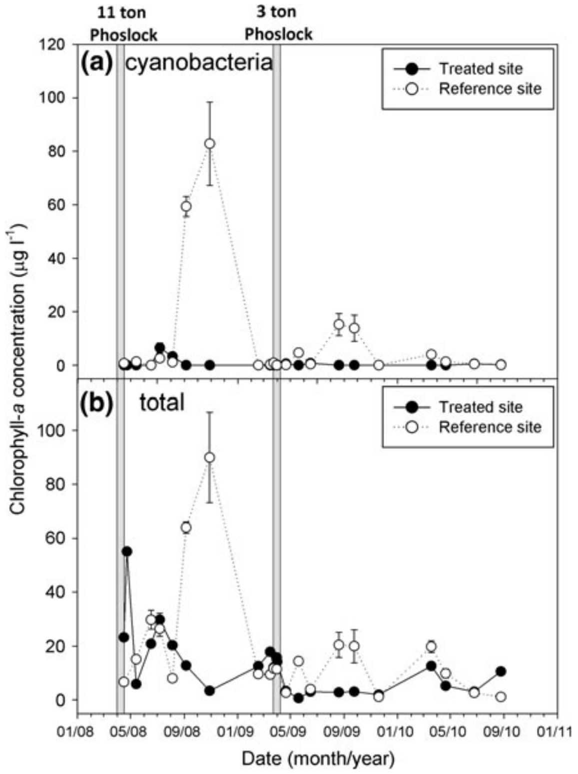

Fig. 2 Course of the cyanobacteria chlorophyll-*a* concentration (μg l^{-1}, **a**) and total chlorophyll-*a* concentration (**b**) in a Phoslock®-treated site, a 5-ha *claustrum* closed from the reference by dams (*closed symbols*), and in water from the surrounding untreated reference (*open symbols*). *Error bars* indicate 1 SD from three subsamples. Also included are the two moments of Phoslock® application (*gray bars*)

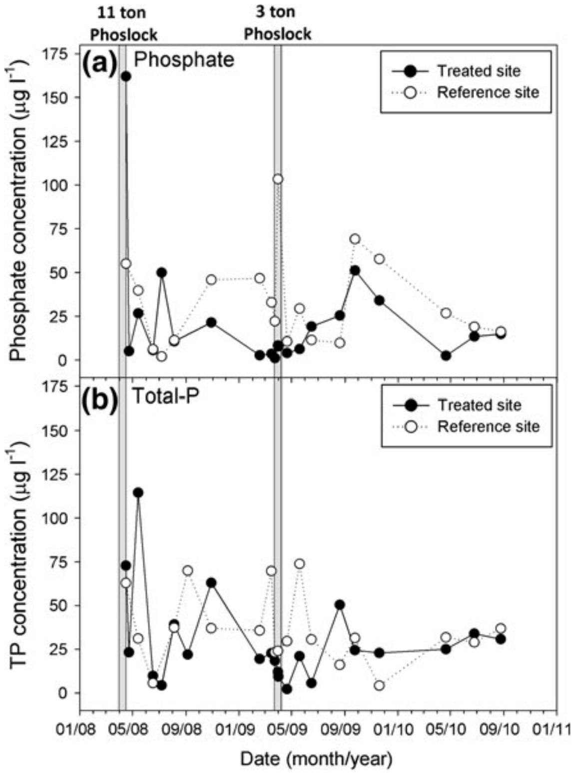

Fig. 3 Course of the phosphate concentration (μg l^{-1}, **a**) and total phosphorus concentration (TP, **b**) in a Phoslock®-treated site, a 5-ha *claustrum* closed from the reference by dams (*closed symbols*) and in water from the surrounding untreated reference (*open symbols*). Also included are the two moments of Phoslock® application (*gray bars*)

claustrum and 9.0 (±21.4) in the surrounding lake. Also total chlorophyll-*a* concentrations over the entire sampling period were lower in the *claustrum* (12.6 ± 12.2 μg l^{-1}) than those in the surrounding lake (18.0 ± 21.5 μg l^{-1}). The mean cyanobacteria chlorophyll-*a* concentrations significantly differed ($F_{1,22} = 6.97$; $P = 0.016$), between *claustrum* and surrounding lake, but this was not true for total chlorophyll-*a* concentrations ($F_{1,22} = 2.22$; $P = 0.151$) at these two sites. In 2009 and 2010, no cyanobacteria blooms occurred in the reference water body.

Over the course of the monitored period PO_4-P and TP concentrations were similar in *claustrum* and reference (Fig. 3; Table 1). However, TN was significantly higher in the reference water than in the treated site, mainly due to significantly higher NO_2/NO_3-N concentrations at the reference site (Table 1); NH_3-N concentrations were similar in both sites. Total lanthanum concentrations increased after each of the two Phoslock® applications, but decreased rapidly to values below 10 μg l^{-1} (Fig. 4). Both total and filterable lanthanum concentrations, were significantly higher in the treated water than at the reference site (Table 1). However, the latter fraction remained below the Dutch Standard of 10.1 μg l^{-1} (Fig. 4; Table 1). All other water quality variables measured, turbidity (NTU), pH, temperature (°C), and oxygen concentration (mg l^{-1}), were similar in the two sites (Table 1). Electrical conductivity (EC, μS cm^{-1}) was significantly higher in the reference water than in the *claustrum* water (Table 1). EC increased slightly over time in the reference, but linear regression analysis revealed that the slope did not differ from zero ($F_{1,19} = 4.02$; $P = 0.059$). In the *claustrum*, the slope (−0.05 ± 0.02 μS cm^{-1} d^{-1}) deviated significantly from zero ($F_{1,21} = 5.62$; $P = 0.027$). The slopes of

Table 1 Mean of water quality variables (±1 SE) over the entire monitoring period April 2008–August 2010 in water from the Phoslock®-treated site and the reference site, including *F*- and *P*-values of rmANOVAs (data of total lanthanum were $\log(x + 1)$ transformed prior to analysis to fulfill homogeneity requirements)

Variable	Treated site	Reference site	*F*-values	*P*-values
Temperature (°C)	14.7 (1.3)	14.0 (1.5)	$F_{1,20} = 0.61$	0.444
Oxygen (mg l^{-1})	10.8 (0.4)	11.8 (0.6)	$F_{1,20} = 4.40$	0.050
EC (µS cm^{-1})	376 (6)	445 (8)	$F_{1,22} = 74.6$	**<0.001**
Turbidity (NTU)	6.6 (1.5)	7.1 (2.2)	$F_{1,22} = 0.05$	0.824
pH	8.4 (0.1)	8.4 (0.1)	$F_{1,22} = 0.29$	0.599
PO_4^{3-} (µg l^{-1})	22.6 (7.7)	32.4 (5.9)	$F_{1,20} = 0.79$	0.387
TP (µg l^{-1})	29.4 (5.6)	35.8 (4.6)	$F_{1,20} = 0.25$	0.623
NO_2^-/NO_3^- (mg l^{-1})	0.27 (0.06)	3.07 (0.20)	$F_{1,20} = 294.6$	**<0.001**
NH_4^+ (mg l^{-1})	0.05 (0.02)	0.06 (0.01)	$F_{1,20} = 0.04$	0.850
TN (mg l^{-1})	0.68 (0.12)	2.45 (0.19)	$F_{1,20} = 201.0$	**<0.001**
Filterable La (µg l^{-1})	0.55 (0.15)	0.17 (0.19)	$F_{1,21} = 10.5$	**0.005**
Total La (µg l^{-1})	31.1 (17.7)	0.40 (0.14)	$F_{1,22} = 58.5$	**<0.001**

Significant differences ($P < 0.05$) between treated and reference site are indicated in bold

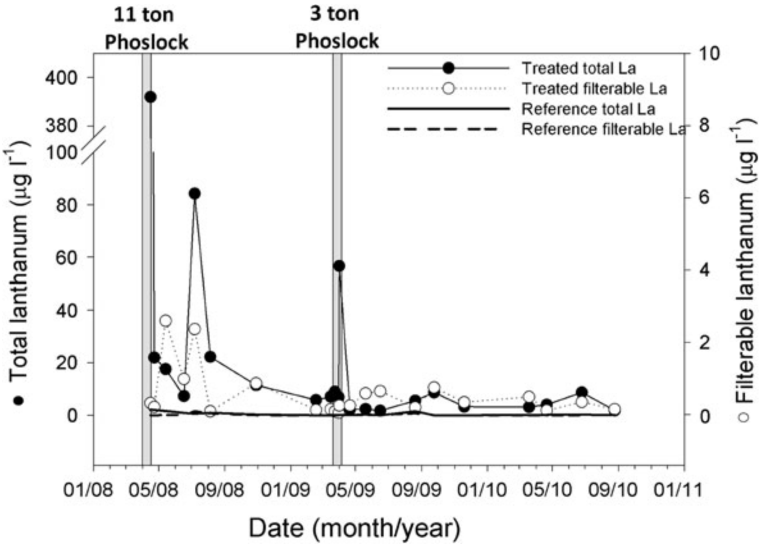

Fig. 4 Course of the total lanthanum concentration (µg l^{-1}, *closed symbols*) and filterable lanthanum concentration (*open symbols*) in a Phoslock®-treated site, a 5-ha *claustrum* closed from the reference by dams (*closed symbols*). Also included are the two moments of Phoslock® application (*gray bars*) and the lanthanum concentrations in water from the surrounding untreated reference (*bold solid and dashed line*)

both lines differed significantly from each other ($F_{1,40} = 9.26$; $P = 0.004$).

Canada Geese (*Branta canadensis*) are very abundant in the area, especially during winter months. Hundreds of geese gathered in De Gouden Ham area annually, and during February–April 2009 and March–April 2010, on average 52 (±10, 1 SD) geese were counted on the water of the *claustrum*, while several dozens were on its shore. Frequently, a few to more than one hundred ducks (*Anas platyrhynchos*) and coots (*Fulica atra*) were observed in the *claustrum*. The 16 geese droppings that had been analyzed for nutrients and lanthanum contained between 0.9 and 3.3 mg PO_4-P per gram dry weight, between 6.6 and 19.3 mg NH_3-N per gram dry weight, and between 0.03 and 69.5 µg lanthanum per gram dry weight. Mean concentrations (±1 SD) were 2.0 (±0.7) and 11.9 (±3.2) mg g^{-1} for PO_4-P and NH_3-N, respectively, and 4.9 (±17.2) µg g^{-1} for lanthanum.

Discussion

In 2008, cyanobacteria bloomed in the surrounding water of De Gouden Ham, and a scum was formed at the north of this surrounding lake, while the *claustrum* Het Groene Eiland remained devoid of cyanobacteria blooms after its isolation from the surrounding water body. Hence, it seems that the lake's owner took the right step to build the *claustrum* and to reduce the internal loading based on the recommendations in the literature (Carpenter et al., 1998; Gulati & Van Donk, 2002; Søndergaard et al., 2003; Welch & Cooke, 2005; Carpenter, 2008; Mehner et al., 2008; Schindler et al., 2008). However, the effect of the formation of the *claustrum* was not studied long enough, i.e., for at least one season after it was formed. Separating the effects of isolation and that of Phoslock® addition on its role in P-fixation to the sediment are difficult. Nonetheless, some inferences can be drawn.

Although several studies have shown effective P absorption by Phoslock® (Douglas et al., 1999, 2004; Robb et al., 2003; Ross et al., 2008; Finkler Ferreira & Da Motta Marques, 2009; Haghseresht et al., 2009; Van Oosterhout & Lürling, this volume), the application of Phoslock® to the *claustrum* did not cause a significant decrease in PO_4-P and TP concentrations. This is also supported by independent measurements of the Institute Dr Nowak and Phoslock Europe GmbH.[8] Nevertheless, the PO_4-P concentration had initially dropped after the first Phoslock® application, but it is not clear if the start PO_4-P concentration was determined accurately. The initially high PO_4-P concentration did not match with the TP analysis (see Fig. 3). This might be due to small colloidal particles, especially from clay, which could have caused an overestimation of the molybdate-reactive phosphorus concentrations (Koopmans et al., 2005). This possibility cannot be ruled out, as the sample was taken slightly after start of the application and turbidity of the water had already increased from 3 to 9 NTU, but then it remains unclear why this was not observed in the TP analysis. Hence, the alternative explanation of an analytical error seems more plausible, also as independent PO_4-P measurements on the same day by the Institute Dr Nowak (before the application) revealed concentrations below the detection limit of their method (i.e., <10 µg l^{-1}), but TP concentrations of 68 µg l^{-1}, which is similar to ours (i.e., 73 µg l^{-1}). A second application with 3.1 tons of Phoslock® was carried out on March 31, 2009, but PO_4-P concentrations increased gradually after the application in March from 8 to 51 µg l^{-1} in September 2009 (Fig. 3).[9]

The first application had a dose of ca. 220 g Phoslock® m^{-2}, which is close to the recommended dose of 250 g m^{-2} for sediment capping in natural conditions (Phoslock® Water Solutions, 2006; Ross et al., 2008) and comparable with the 270 g Phoslock® m^{-2} used in Clatto Reservoir (Meis et al., 2012). Sediment P fractionation data gathered by the Institute Dr Nowak and Phoslock Europe GmbH revealed that the Phoslock® application reduced the freely available P-pool in the sediment by about 50% (from 0.4 to 0.2 mg P kg^{-1} dry sediment[10]), where complete removal could be expected from the dose applied. A month after application, the total mobile P-pool was hardly affected by the Phoslock® application; the mobile P-pool was reduced from 27.2 to 24.1%,[11] which is comparable with the effect of Phoslock® application in Clatto Reservoir. In Clatto Reservoir, Phoslock® caused some reductions in the mobile P pool, but did not significantly alter the mobile P-pool over a 4-week post-application period (Meis et al., 2012).

The total amount of Phoslock® applied exceeded—by far, the amount needed to bind all P in the water column. The fact that the PO_4-P and TP pools in the water column seemed unaffected may be explained by several mechanisms. First, based on the high dose that was applied and the reaction time needed for Phoslock® to bind PO_4-P (van Oosterhout & Lürling, this volume), we can safely say that reaction time was adequate, but Phoslock® will not remove particulate P, or P in organisms such as algae. Second, the effectiveness of Phoslock® is reduced by interference of naturally occurring oxyanions other than phosphate (Johannesson & Lyons, 1994) or complex-forming

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[8] http://static.phoslock.eu/Upload/pdf-documents/Interim_Report_Het_Groene_Eiland_November_08.pdf, http://static.phoslock.eu/Upload/pdf-documents/Portfolio_HGE.pdf.

[9] http://static.phoslock.eu/Upload/pdf-documents/Portfolio_HGE.pdf.

[10] http://static.phoslock.eu/Upload/pdf-documents/Interim_Report_Het_Groene_Eiland_November_08.pdf.

[11] http://static.phoslock.eu/Upload/pdf-documents/Interim_Report_Het_Groene_Eiland_November_08.pdf.

humic substances (Tang & Johannesson, 2003, 2010; Sonke & Salters, 2006). Inasmuch as the overall PO_4-P and TP concentrations were only 30 and 18% lower in the *claustrum* compared with the reference site, both above mentioned reasons could have contributed to the Phoslock®-binding capacity being less than expected. Over longer periods also, ongoing inputs of P might have played a role.

Because the effect of Phoslock® application on reducing the internal loading to water column seems unclear, one may argue that the Phoslock® layer was unevenly distributed—or parts of the sediment remained uncovered, which will allow release of redox-sensitive bound P into the water column. The application was performed from a GPS-coordinated barge, which assures the application covers the entire water surface. As the distribution of the Phoslock® layer was not measured—e.g., by means of sediment traps or lanthanum measurements in sediment samples, we can only speculate on its distribution over the lake's sediment. If an uneven distribution did occur, then this would most likely have been because of wind-driven water movements.

The PO_4-P-binding capacity of lanthanum does not seem to be affected by altered redox conditions (Ross et al., 2008). However, the recent study of Meis et al. (2012) revealed that saturated Phoslock® could release up to 21% of the bound P, of which 14.4% was redox-sensitive bound-P. Hence, the observed summer anoxia that occurs near the sediment[12] in this shallow lake could not be excluded as the causal factor for release of labile P. After the 2nd application, water column PO_4-P concentrations increased from 8 to 51 $\mu g\ l^{-1}$. This increase of 43 $\mu g\ l^{-1}$ would make with an estimated water volume of 130,000 m^3 in the *claustrum* a total of 5.6 kg P that could have originated from the total targeted 141 kg P (i.e., 110 and 31 kg P after the 1st and 2nd applications) if 14% (cf. Meis et al., 2012) of it was redox-sensitive bound-P. However, we did not conduct phosphorus release experiments before and after the application under oxic and anoxic conditions, making it difficult to decipher whether reductant-soluble-P was involved and, if so, to what extent. However, the *claustrum* could also be hydrological poorly isolated from its underground water inputs and thus experiencing strong P-rich groundwater inflow or other sources of P-input, such as from water birds.

Although occasionally several ducks and coots were observed on and near the *claustrum* during summer, by far, most birds were migrating Canada geese that visit the lake for a few months each winter. Faeces analysis revealed mean PO_4-P concentrations of 2 $mg\ g^{-1}$ dry feces, which is in agreement with the literature data on geese droppings (Van Geest et al., 2007; Ayers et al., 2010). Assuming that a Canada goose daily produces 80 g dry weight of droppings (Scherer et al., 1995), then on average, daily more than 4 kg of droppings are produced around the lake. With 2 mg PO_4-P g^{-1} dry faeces and the geese staying around the lake for 100 days, the total PO_4-P contributed from the droppings will be around 830 g. If all enter the lake and all food has been collected elsewhere, then P from the geese input might annually increase water P concentrations by 6 $\mu g\ P\ l^{-1}$ (i.e., 830 g to 130,000 m^3). However, not all droppings will enter the *claustrum* and not all food will be collected outside the *claustrum*, which is clearly reflected in some droppings that contained a relatively high mass fraction of lanthanum. This lanthanum could have originated not only from sediment particles attached to the plants, but also from lanthanum taken up by the plants, as has been observed for duckweed that bioconcentrated lanthanum 138 times from the water (Yang et al., 1999). Nonetheless, the annual visit of the geese is a source of nutrients, and with Canada goose being one of the most rapidly increasing bird species in the Netherlands (Koffijberg et al., 2010), increasingly more nutrient input from foraging in surrounding agricultural areas to the water of the *claustrum* might be expected.

The TN and nitrate concentrations were significantly lower in the *claustrum* than in the reference water. In the *claustrum*, rapidly dense *Elodea nuttallii* beds were formed, which could have depleted the nitrate concentrations (Ozimek et al., 1990) and forced a shift to clear water through N limitation of periphyton and filamentous algae on plant surface and phytoplankton (Jeppesen et al., 2007). It has been established that in Northern temperate shallow lakes, the shift from clear water to a more turbid state with low plant biomass occurs at TN between 1.2 and 2 mg N l^{-1} (González Sagrario et al., 2005). TN in the *claustrum* was below this concentration range; however, in the reference almost the entire year,

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[12] http://static.phoslock.eu/Upload/pdf-documents/Interim_Report_Het_Groene_Eiland_November_08.pdf.

TN exceeded this threshold range for submerged macrophyte dominance.

The TN:TP molar-ratio was on average 16 in the *claustrum* and 58 in the reference, and there was no clear trend in either water. Lake water with a TN:TP ratio below 20 can be considered N-limited, while water with a ratio above 38 might be P-limited (Kosten et al., 2009). Hence, the water in the *claustrum* could not be characterized as being P-limited. Mean TP concentrations in both the *claustrum* and the surrounding water were around the mesotrophic–eutrophic boundary of 35 μg l^{-1}, which is below the ca. 50 μg P l^{-1} in Danish shallow lakes, which marked the transition between the state with clear water dominated by macrophytes and the level above which also a turbid algal dominated state is possible (Jeppesen et al., 1990). During the sampling period, the water in both *claustrum* and reference could not be classified as turbid, phytoplankton dominated. However, also in mesotrophic lakes, wind-driven cyanobacteria scum accumulation may occur at certain near-shore sites, while open water might be quite clear (Johnston & Jacoby, 2003). Also in De Gouden Ham system, such surface scums may be formed from relatively low water column cyanobacteria concentrations, drift downwind, and accumulate at lee shores, such as the Molenstrand area in 2008, or in sheltered bays such as the former Groene Eiland bay.

The EC in the reference water was comparable with water of River Maas EC (Van den Brink et al., 1993), but it decreased gradually in the *claustrum* pointing toward a diminishing influence of River Maas water that feeds De Gouden Ham.

In conclusion, over the entire monitoring period, mean PO_4-P and TP concentrations were only marginally lower in the *claustrum* compared with the reference site, which places severe doubts on the efficacy of the modified clay in controlling P in this system. TN concentrations were reduced by 73% in the *claustrum* through abundant growth of submerged vegetation. The creation of a 5-ha *claustrum* had a positive outcome on the recreation area, as no swimming bans had to be issued because cyanobacteria did not exhibit increased growth as well as there was no inflow of surface scum from the surrounding water body in three consecutive summers. The cyanobacteria chlorophyll-*a* concentrations that resulted were significantly lower in the *claustrum* than in the reference water. However, the enclosed recreation area could also experience gradual increase in P concentrations. Already after 1 year of Phoslock® application, a reapplication of 3.1 tons Phoslock® was needed, and with annual inflow of P, sustainability of the effect of measures is questionable.

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