Spring Valley Lake Association
Operations Report
June 25, 2019

Facilities, Maintenance and Grounds:

Equestrian Estates

- Set up 3 events at the EQ during this past month.
- Repaired water main break at Longacres park, cause by a residents contractor, incident reports have been made and contractor will be billed.
- We are requesting engineering inspections of our 4 Equestrian bridges, these are up on our reserve and this is the first step.
- Added sand to stall 24
- Repaired fly spray system issues in stalls
- Conducted weekly stall safety inspection at the stalls
- All arenas have daily dragging as scheduled.
- Performed all scheduled daily duties
- Regular and emergency work orders performed through-out EQ

Buildings

- Regular and emergency work orders performed though-out the SVLA buildings.
- Set up for 10 events lake side.
- Installed replacement bulletin board at our AO parking lot, which required installing 110v to the bulletin board.
- Repair broken kitchen drawers
- Safety inspections have been completed weekly.
- Fire extinguisher inspections are completed which is done monthly.

Meadowlark Park project phase 2

- DG has come in and is being installed.
- Contractor is looking into alternative solution as the backstop has been on order for over 4 months and some items are back ordered and delaying final delivery.
- The walking trail will be opened for use by our Family Festival on June 29, 2019.

Marina Picnic area project

- Installation of paving stones is complete.
- This project has slowed process to take care of a couple issues, 1 – permit to repair and or replace the existing sidewalk, 2 – incorporate the approved first uv filter system in this area.

  1 – working with the county on the repairs, the County has added this area to their repairs this summer and will be repairing the sidewalk

  2- the location of the new uv filter system has been designated and the enclosure, electrical and filter will be installed and running by the second week of July.
- This area will remain closed during the firework show.
- Renderings of final designs will be submitted

Grounds

- Regular work order performed at grounds, restrooms, etc., as required.
- Irrigation repairs at all grass areas as needed.
- Replaced damaged Solar panel, damaged by a delivery truck, an incident report was made.
- Ongoing weed abatement at all lake side properties including center median all included (29 acres and 1.5 mile median)
- Our weed abatement program has started another year, this program allows owners of unimproved lots to use our contractor to keep weeds in requirement of San Bernardino County code 23.0305 and our SVLA Architectural policy and procedures 6.5 at a fixed yearly fee of $195/year for standard 7,200 sq.ft. or less lots and $205/year for larger lots. The lots are maintained from June 1, 2019 to May 31, 2020 on this new current program. We currently have 141 of the 308 unimproved lots on the program to date.

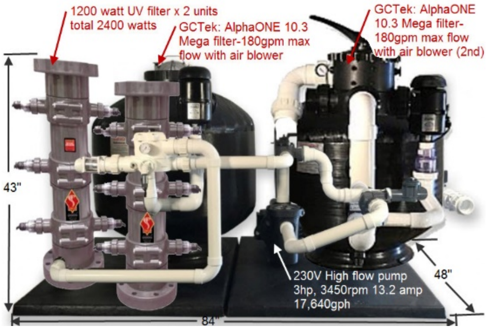
Lake and Fishing Areas:

Marina/ Lake

- Added 100 tons of sand to the beach area this is a yearly maintenance done to keep up with sand lost throughout the year.
- Buoy replacement is complete
- Lake Siren was tested and is operational.
- Daily dragging and inspections of the beach have started and will continue through the summer.
- Preparations are being made for this year's firework show and family festival. Festival will be held on the north section of the park this year. We are adding temporary lighting for added safety during exiting from the beach area and parking lots.
- It is imperative that no boats start moving on the lake until the all clear LAKE SIREN has been sounded after the firework show. Violators could be cited and this could affect the fire marshal allowing vessels on the water during the firework show in the future.
- There was some sand removed from the west side of the dam by someone that most likely started out as an innocent sand castle size river but quickly turned into a 10' wide 12" deep river that flowed over 1,000 gallons per minute out of our swim area. This little diversion changed the direction of our outflow from the swim area moving 12 tons of sand into the lake bottom. Attached are pictures of the area and flow, this was repaired.

UV filter

- The first UV filter components are on order, we have received some parts to date and expect to have this first unit up and running and the second unit ordered by the second week of July. We will post and document the results.



NPDES permit

- We have gathered the necessary information and turned in the required forms to Russel Normal the Water Resource Control Engineer at Lahontan Regional Water Quality Control Board, Forms 200, form 1 and Form 2E, along with technical information from Sepro the only supplier for Phoslock which is one of the treatments we are trying to get on this NPDES permit. We are waiting for feedback from Lahontan.
- We have reached out to 4 consulting agencies to get assistance on this permit since last year. And during this course of information we have determined it would be beneficial to remove Alum and the muck reducer from the permit to help expedite its approval. The forms listed above were turned in following this advice. Once the permit is granted we can work on an addendum to the permit for Alum and or muck reducer.
- I have attached the email and supporting technical information from Ajay R. Jones P.C.A, Aquatic Technical Specialist Southwest Region (CA, AZ, NV, HI) at SePRO Corporation for your review. This is the information attached to the forms to Lahontan.
- I have attached a letter from Curtis Cress, Branch Manager/Aquatic Biologist at Marine Biochemists/Innovative Water Care LLC who spoke to Russel Normal on our behalf regarding the NPDES permit and requirements for Alum. Summary the testing required will take time, we will work on proposals for the testing for budgeting, but it has been suggested by Curtis that it will be thousands of dollars and months of work.
- I have attached an email and letter that was submitted to Russel Norman at Lahontan from Terry McNabb, CLM, Manager/Aquatic Biologist/Certified Lake Manager at Aquatechnex. This was Aquatechnex approach for putting Lahontan on notice regarding our intended treatment of our water, also attached is an email towards his thinking of this approach. After Russell at Lahontan received this email, I confirmed to Russel this is not our intent now to get a CEQA permit started now as we are focused on the NPDES permit, I have added this email to show you the process we have been involved in to this point.
- We have also been in contact with Dawn Bachelor and Ben Chen from Solitude Lake Management who is currently applying Phoslock to a lake under a NPDES permit in San Diego. This contact led me to Blankenship & Associates who is working on a proposal for use on assisting us with the NPDES permit process. Blankenship & Association did the permit for Solitude Lake Management under San Diego Reginal Water Quality Control Board, we have yet to receive any further information from Blankenship & Associates at this time.

From: Jones, Ajay <ajones@sepro.com>
Sent: Thursday, June 06, 2019 12:32 PM
To: Dennis Teece
Subject: Spring Valley Lake documents for E2
Attachments: Spring Lake Dennis Phoslock.pdf; Phoslock Technical Overview updated.pdf; Bishop et al Phoslock Laguna Niguel 2014.pdf; Spears et al 2015_ 16 case studies.pdf; Dithmer et al. 2016_Published article.pdf

Hey Dennis see attached. I would submit these documents with the form E2, if EPA doesn't accept it I would be surprised because they aren't offering you any sort of example – I expect they don't exactly know what they need, but just need some info if you are able to provide it. The spears paper is great cedidental to accompany the Technical overview and the overview we provided (Spring Lake Dennis Phoslock).

Last year the EPA came out with additional regulations on alum in regards to being a non-essential metal and having toxicology on fish at certain concentrations., see links below.

https://www.epa.gov/wqc/aquatic-life-criteria-aluminum

https://www.epa.gov/sites/production/files/2018-12/aluminum-criteria-calculator-v20.xlsm

Ajay R. Jones P.C.A | Aquatic Technical Specialist Southwest Region (CA, AZ, NV, HI)

SePRO Corporation
Sacramento, CA | www.sepro.com

661-381-8384 Mobile

ajones@sepro.com

Phoslock®

Overview

Phoslock® is a patented phosphorus locking technology containing lanthanum (5%) embedded inside a clay matrix (~95%). Phoslock® was specifically developed to bind phosphorus in surface water by the Australian national science agency, Commonwealth Scientific and Industrial Research Organization. Phoslock® is widely used globally and SePRO Corporation provides technical support and distribution in the United States. Phoslock® is highly specific to binding phosphorus, does not directly impact water chemistry, and is safe for humans and wildlife. The ultimate fate of bound phosphorus is in a non-bioavailable mineral called Rhabdophane and this transitions to become more tightly bound through time. After binding phosphorus, the bond is essentially permanent under any typical environmental conditions and more tightly bound than other technologies. Over 70 peer-reviewed publications exist on Phoslock® with many more in process that specifically address efficacy, fate, longevity and non-target impacts. Phoslock® has received US and Canadian NSF/ANSI Standard 60 Certification for use in drinking water. This accreditation was provided by the Water Quality Association of the United States (WQA), an independent accreditation agency authorized by the US Environmental Protection Agency (https://www.wqa.org/find-products/ctl/detail/mid/1054/cid/sepro_corporation/sid/6/keyword/phoslock accessed 11.16.18)

Demonstrated Successes

Phoslock® is unaffected by site specific water conditions (Ross et al. 2008) and is highly specific to binding phosphorus. Phoslock® binds to phosphorus and is extremely efficient with a calculable ratio of 100 pounds of Phoslock® to bind 1 pound of phosphorus (1:1 La:P molar ratio). This ratio is based on the consistent documented binding specificity and capacity of Phoslock®, even in disparate water types (Reitzel et al. 2013). The lanthanum-phosphate complex is highly insoluble and can form with low concentrations of reactants over a wide range of pH levels (Haghesereshtt et al. 2009). The efficiency of phosphate precipitation by lanthanum is greater than that of other salts (i.e. iron, aluminum) and the solubility product constant is more tightly bound and stable under differing environmental conditions (Firsching and Brune 1991; Ross et al. 2008). Upon application to water, lanthanum associated with the clay in Phoslock® preferentially and rapidly binds with phosphate (PO_4), forming a highly stable and non-bioavailable mineral called rhabdophane ($LaPO_4 \cdot H_2O$; Jonasson et al. 1988). Rhabdophane further transforms to a more stable mineral, monazite ($LaPO_4$), through time (Cetiner et al. 2005; Dithmer et al. 2015).

Hundreds of large-lake systems throughout world have been treated with Phoslock and numerous smaller water bodies are additionally treated throughout the US annually. See a list of some projects in the United States and worldwide easily available per this link https://sepro.com/aquatics/phoslock. Specific project details are included in each case study. Two case studies have been provided in the appendix that outline successful US applications of this technology. Additionally, over 70 peer-reviewed publications are present on this technology. See some references below on how it can improve water quality. Papers can be provided upon request. For field studies, site details are in each publication.

Bishop, W.M., R.J. Richardson. 2018. Influence of Phoslock on legacy phosphorus, nutrient ratios and algal assemblage composition in hypereutrophic water resources. *Environmental Science and Pollution Research* 25: 4544-4557.

Bishop, W.M., S. Hyde, T. McNabb, I. Cormican, B.E. Willis. 2014. Operational evaluation of Phoslock phosphorus locking technology in Laguna Niguel Lake CA. *Water Air and Soil Pollution*. 225(2018): 1-11.

Epe, T.S., Finsterle, K., Yasseri, S., 2017. Nine years of phosphorus management with lanthanum modified bentonite (Phoslock) in a eutrophic, shallow swimming lake in Germany.Lake Reserv. Manag. 33:119–129.

Meis S, Spears BM, Maberly SC, O'Malley MB, Perkins RG (2012) Sediment amendment with Phoslock in Clatto Reservoir (Dundee, UK): investigating changes in sediment elemental composition and phosphorus fractionation. Journal of Environmental Management 93:185-193

Reitzel K, Andersen FO, Egemose S, Jensen HS (2013) Phosphate adsorption by lanthanum modified bentonite clay in fresh and brackish water, Water Research 47(8):2787-2796

Reynolds CS (1972) Growth, gas vacuolation and buoyancy in a natural population of a planktonic blue-green alga. 2(2):87-106

Robb MS, 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

Spears BM, Mackay EB, Yasseri S, Gunn IDM, Waters KE, Andrews C, Cole S, De Ville M, Kelly A, Meis S, Moore AL, Nürnberg GK, van Oosterhout F, Pitt JA, Madgwick G, Woods HJ, Lürling M (2016) A meta-analysis of water quality and aquatic macrophyte responses in 18 lakes treated with lanthanum modified bentonite (Phoslock®)" 97:111-121

Van Oosterhout, J. F. X. &M. Lürling, Phosphorus binding clay (Phoslock) in mitigating cyanobacterial nuisance: effects on water quality variables and plankton. Hydrobiologia 710 (1) 265-277 (2013).

Egemose, S., K. Reitzel, F. Ø. Andersen & M. R. Flindt, Chemical lake restoration products: sediment stability and phosphorus dynamics, Environment Science & Technology 44 (3), 985-991 (2010)

Effects of Treatment

Treatment Safety

To assess and manage possible environmental impacts of a product, it is important to understand the potential risks associated with its use. The objective of the following information is to describe existing toxicity data on the product and assess any potential risks to the aquatic environment. Typical Phoslock application rates are < 150 mg/L. Phoslock applications may occur as a single event or over several days and also may be split over a season or multiple seasons depending on the site and management objective.

When Phoslock is applied to water, lanthanum associated with the clay in Phoslock preferentially and rapidly binds with phosphate (PO_4), forming a highly stable mineral called rhabdophane ($LaPO_4$). This resulting rhabdophane complex has a very low solubility ($K_{sp} < 10$-27) and is not influenced by changes in pH and redox reactions in waterbody sediments, thus is not bio-available. Lanthanum can only be extracted from rhabdophane in the laboratory using strong acid extraction methods. Laboratory studies with Phoslock demonstrated that no lanthanum released within 24 hours when granular Phoslock (10 mg/L) was dissolved in de-ionized water; and only a small concentration of lanthanum (~0.016 mg/L or 3% of the total lanthanum in Phoslock) was released from the 10 mg/L concentration of Phoslock when dissolved in low alkalinity natural water or synthetic soft water (Yasseri and Nowak 2008).

The margin of safety associated with lanthanum toxicity is very high, even if the total amount of lanthanum applied to a system following a Phoslock application became readily available in water (which it does not due to the Phoslock formulation and the fact that lanthanum binds to phosphates in water). For example, free lanthanum levels following an application dose of 75 mg/L Phoslock in Barensee Lake, Germany resulted in a peak level of 0.130 mg La^{+3} /L shortly after application and <0.02 mg/L one month later. Toxicity tests from this Barensee Lake project revealed an EC_{50} of 103 mg La^{+3} /L zooplankton (*Daphnia magna*) and EC_{50} of 150 mg La^{+3} /L for fish eggs (Danio rerio). The peak level of La^{+3} detected in the lake following application was approximately 800 and 1,150 times lower than the EC_{50} concentrations for zooplankton and fish eggs respectively. Also, due to the ability of organisms to readily process lanthanum (through the liver) and the low level of free lanthanum that potentially becomes available for a short period of time following Phoslock applications, the aquatic toxicity risk and hazard to aquatic organisms is negligible. While free lanthanum can be used in tests to assess the toxicity to organisms, lanthanum in Phoslock, or bound as rhabdophane, is not free and unlikely to become available or achieve concentrations of toxicological concern in the natural aquatic environment.

There is also a very low potential for human exposure to lanthanum in Phoslock after being applied due to the minimal bio-availability. Even if an exposure occurs, lanthanum is readily processed by the liver and excreted with no negative impacts observed. Lanthanum is used in a prescription drug called Fosrenol® to decrease blood phosphate levels in humans. The Food and Drug Administration approved human dose rate for Fosrenol® is 750 to 3,000 mg/day.

Routes of exposure due to ingestion of water or fish consumption are of minimal risk of lanthanum toxicity (40-400 times lower than approved Fosrenol® daily intake). This information and the previous environmental assessment information is more thoroughly summarized and publicly available at https://www.sepro.com/aquatics/phoslock under technical information (SePRO Corporation 2011).

Numerous standard ecotoxicity studies have been performed on fish, water column invertebrates, and benthic invertebrates which all support a very positive ecotox profile and no predicted toxicity concern at typical and recommended use rates as presented in this proposal. References are listed below for numerous standard studies and peer-reviewed publications regarding safety to receiving systems. Individual studies can be provided upon request and results should support that no additional testing is required for this project.

Bishop, W.M., S. Hyde, T. McNabb, I. Cormican, B.E. Willis. 2014. Operational evaluation of Phoslock phosphorus locking technology in Laguna Niguel Lake CA. Water Air and Soil Pollution. 225(2018): 1-11.

Clearwater SJ. 2004. Chronic exposure of midge larvae to Phoslock. NIWA (National Institute of Water & AtmosphericResearch). Prepared for Ecowise Environmental Pty Ltd. NIWA Client Report No. AUS2004-005, August 2004.

Clearwater SJ and CW Hickey. 2004. Ecotoxicity testing of Phoslock on sediment-dwelling aquatic biota and rainbow trout.NIWA (National Institute of Water & Atmospheric Research). Prepared for Ecowise Environmental Pty Ltd. NIWA Client Report No. AUS2004-004, June 2004.

ECOTOX Report. 2008. Toxicity assessment of Granulated Phoslock® to the Cladoceran Ceriodaphnia dubia. Report prepared for Phoslock Water Solutions Ltd. ECOTOX Services Australasia, July 2008.

ECOTOX Report. 2006a. Toxicity assessment of two Phoslock® formulations to the eastern Rainbow fish. Hydrobiology Pty Ltd, ECOTOX Services Australia. March 2006.

ECOTOX Report. 2006b. Toxicity assessment of Phoslock® to the freshwater shrimp Macrobrachium sp. Hydrobiology Pty Ltd, ECOTOX Services Australia. November 2006.

Lurling M., Tolman Y. 2010. Effects of lanthanum and lanthanum-modified clay on growth, survival and reproduction ofDaphnia magna. Water Research. 44(1):309-19

Martin M.L., and C.W. Hickey. 2004. Determination of HSNO ecotoxic thresholds for granular Phoslock (Eureka 1 formulation) phase 1: Acute toxicity. NIWA (National Institute of Water & Atmospheric Research) Client Report No. HAM2004-137, October 2004.

Stauber J.L. 2000. Toxicity testing of modified clay leachates using freshwater organisms. CSIRO Centre for Advanced Analytical Chemistry Energy Technology. Report No. ET/IR267R. Prepared for CSIRO Land and Water. March 2000.

Stauber J.L. and M.T. Binet. 2000.Canning River Phoslock field trials – Ecotoxicity testing final report.CSIRO Centre forAdvanced Analytical Chemistry Energy Techniology. Report no. ET317R. Prepared for CSIRO Land and Water and the WA Water and Rivers Commission. August 2000.

Watson-Leung T. 2009. Phoslock Toxicity Testing with three Sediment Dwelling Organisms (Hyalella azteca, Hexagenia spp.and Chrinonomus dilutes) and Two Water Dwelling Organisms (Rainbow Trout and Daphnia magna). Aquatic Toxicology Unit,Ontario Ministry of the Environment, Ontario, Canada.

Long Term Effects and Water Uses

No unintended long-term effects in waterbodies from lanthanum in Phoslock are predicted. Lanthanum is designed in the formulation to not be readily dissolved in the water-column though to rapidly bind with free phosphorus and transition to a stable mineral in the sediments. For example, free lanthanum levels following an application dose of 75 mg/L Phoslock in Barensee Lake, Germany resulted in a peak level of 0.130 mg La^{+3} /L shortly after application and <0.02 mg/L one month later. Publications from numerous lake applications have documented the fate of lanthanum in both the water and sediments per below references.

Dithmer L, Nielsen UG, Lürling M, Spears BM, Yasseri S, Lundberg D, Moore A, Jensen ND, Reitzel K (2016) Responses in sediment phosphorus and lanthanum concentrations and composition across 10 lakes following applications of lanthanum modified bentonite. Water Res. 97:101-110

Spears BM, Lürling M, Yasseri S, Castro-Castellon AT, Gibbs M, Meis S, McDonald C, McIntosh J, Sleep D, Van Oosterhout F., Lake Responses following lanthanum-modified bentonite clay (Phoslock) application: an analysis of water column lanthanum data from 16 case study lakes, Water Research, 47 (15), 5930-42 (2013)

The longevity of phosphorus reduction in a waterbody is dependent upon phosphorus availability and abundance, Phoslock dosing, and the phosphorus budget of the treatment site. With dosing that reduces phosphorus from high to low levels, multiple water quality parameters may drop below established water quality standards. Trophic status of the waterbody may change with high enough doses of Phoslock. Meeting established water quality standards may restore or increase the number or water uses designations such as drinking, recreation, and for wildlife.

Lake Ecology

Many cyanobacteria are not readily grazed by zooplankton and do not move up the food chain to support a healthy fishery (Webster and Peters 1978; Lampert 1981,1987; Reinikainen et al. 1995) and one reason why blooms of extreme densities are commonly observed. Also, some cyanobacteria directly negatively impact cladoceran growth, health and fecundity (Aloysio da S Filho et al. 2008; Zagatto et al. 2012). Additionally, types of cyanobacteria can also clog zooplankton filtering structures, have poor digestibility and cause toxin accumulation in zooplankton (if consumed; Lampert 1987; Reinikainen et al. 1995; Bednarska et al. 2014).

Excessive phosphorus inputs and decreased nitrogen to phosphorus ratios (N:P) have been linked to increased frequency and distribution of toxigenic cyanobacterial blooms (Smith 1983; Seale et al. 1987; Ghadouani et al. 2003; Paerl 1990; Paerl 1991; Hallegraeff 1993; Watson et al. 1997). Phosphorus is required at a threshold amount to support bloom formation in water (Downing et al. 2001; Carvalho et al. 2013) or sediments (Istvanovics et al. 1993; Carey et al. 2008). Schindler et al. (2008) concluded that phosphorus reduction and the stoichiometric ratio of nutrients (N:P) should be the focus of efforts to manage eutrophication in freshwaters.

Phoslock® can specifically remove P and thereby shift the N:P ratio higher, as well as decrease the P levels below thresholds commonly selecting for cyanobacteria (Trimbee and Prepas 1987; Downing et al. 2001). This shift in the N:P ratio and beneficial impact on the algal assemblage has been documented following Phoslock® applications (Bishop and Richardson 2018). That shift to more beneficial algal types should competitively exclude the degree of recovery of cyanobacteria. Selecting for more beneficial types of plankton that readily move up the food chain subsequently support fisheries health. This would be an important ecosystem benefit for the endangered June Sucker in Utah Lake.

Operational Treatment Factors

Phoslock is manufactured in a granule which may be applied as a granule or slurry. Granular application can be made with a variety of mechanical spreaders to fit application scenarios. Granules can be dissolved in water to create a slurry for application. Slurry application in lakes require high agitation/mixing and often utilize high water volume applications with equipment that does not have a restrictive orifice. In practice this can be a gas-powered trash pump that pulls water from the treatment site into a tank or mixing drum where Phoslock is dissolved, then the slurry actively or passively flows back into the treatment area. The application equipment is transported across the treatment site in an adequately sized watercraft. Watercraft size should be optimized for watercraft safety in the waterbody and for applying Phoslock in cost effective manner. Schedules of application for Phoslock are dependent on specific management plans for water quality goals.

Detailed Product Information

Phoslock® is a product only containing lanthanum (5%) embedded inside a bentonite clay matrix (~95%). Phoslock is not considered hazardous by the Occupational Health and Safety Administration (OSHA) Hazard Communication Standard (29CFF 12910.1200). Lanthanum and the clay used in the formulation are not listed on the USEPA Toxic Substances Control Act inventory list. The SDS is available online (https://www.sepro.com/Documents/Phoslock_SDS.pdf accessed 5/31/2019) and provided at the end of this proposal. Phoslock® has received US and Canadian NSF/ANSI Standard 60 Certification for use in drinking water. This accreditation was provided by the Water Quality Association of the United States (WQA), an independent accreditation agency authorized by the US Environmental Protection Agency (https://www.wqa.org/find-products/ctl/detail/mid/1054/cid/sepro_corporation/sid/6/keyword/phoslock accessed 11.16.18)

PHOSLOCK®
Phosphorus Locking Technology

An Overview of Phoslock and Use in Aquatic Environments

What is Phoslock?

Phoslock is a patented phosphorus locking technology containing lanthanum (5%), a naturally occurring earth element, embedded inside a clay matrix (~95%). Phoslock was developed by the Australian national science agency, Commonwealth Scientific and Industrial Research Organization (CSIRO), to remove phosphorus from water bodies and restore water quality. Phoslock is produced through a patented ion exchange process whereby lanthanum ions displace sodium ions within the clay matrix. The formulation process of Phoslock absorbs lanthanum into a non-toxic carrier such that the lanthanum retains its capacity to bind phosphate when applied to aquatic environments and results in a non-toxic mineral that becomes an inert component of the sediments.

For over ten years, Phoslock has been successfully used in water resource restoration programs around the world to remove free reactive phosphorus and restore water quality. Although Phoslock is a new technology to the United States (2010), it is rapidly emerging as the most effective phosphorus inactivation and water quality restoration solution for ponds, lakes and reservoirs.

How does Phoslock work?

Following an application of Phoslock, the lanthanum ions sorbed to the clay matrix react preferentially with free phosphate compounds in water (removing free reactive phosphorus) and rapidly form a highly stable insoluble mineral. The resulting mineral complex becomes integrated as an inert component into the natural sediments of the waterbody and is not bio-available. Due to the specificity of Phoslock to phosphate, as long as binding sites are available, it will continually bind new incoming phosphorus from internal and external sources.

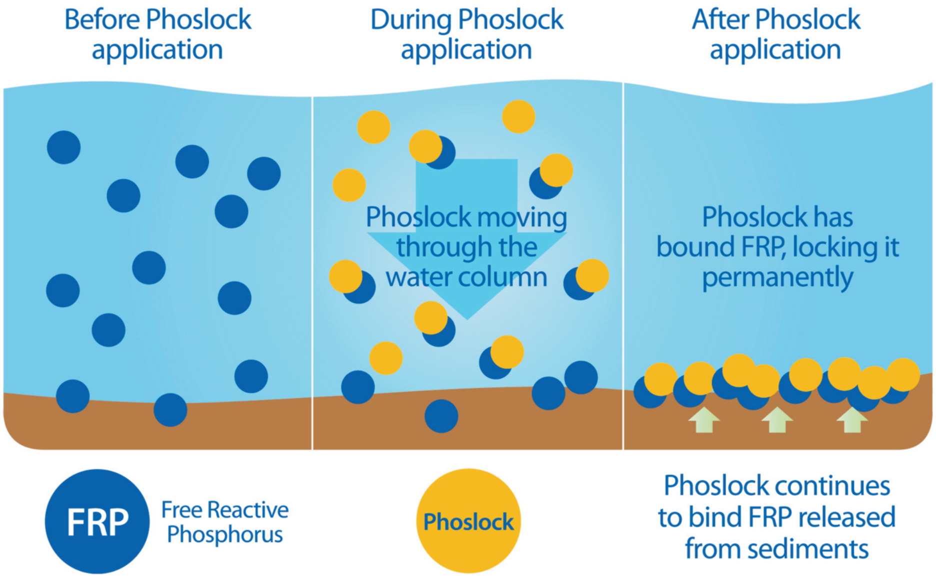


Figure 1. *Illustration of the binding of Phoslock with Free Reactive Phosphorus (via phosphate bond) in water and as it is released from sediments.*

[†] Throughout this document, we use the phrase negligible risk. Risk is the probability of occurrence of an adverse effect from a given exposure to a substance. All substances have an inherent hazard (capacity to cause adverse effects). However, the risk of a potential adverse effect is managed by the product formulation, use directions, application rates and exposure. Phoslock at appropriate uses and dosing will result in negligible or insignificant risk.

Ecological Assessment

To assess and manage possible environmental impacts of a product, it is important to understand the potential risks associated with its use. The objective of the following information is to describe existing toxicity data on the product and assess any potential risks to the aquatic environment. Typical Phoslock application rates are < 150 mg/L. Phoslock applications may occur as a single event or over several days and also may be split over a season or multiple seasons depending on the site and management objective.

Evaluation of Lanthanum Toxicity

Lanthanum is a naturally occurring earth element. Lanthanum can occur in many forms. One such form, lanthanum chloride ($LaCl_3$) can be potentially toxic to aquatic organisms due to the dissolution of high levels of free lanthanum into water after application. This prohibits the use of $LaCl_3$ as an environmentally compatible phosphorus mitigation solution. However, when lanthanum is applied to surface waters in the form of Phoslock, the risk of potential lanthanum toxicity to aquatic organisms is negligible due to the unique formulation of Phoslock (absorbed to the clay matrix) and a limited potential for exposure to free lanthanum. When Phoslock is applied to water, lanthanum associated with the clay in Phoslock preferentially and rapidly binds with phosphate (PO_4), forming a highly stable mineral called rhabdophane ($LaPO_4$). This resulting rhabdophane complex has a very low solubility ($K_{sp} < 10^{-27}$) and is not influenced by changes in pH and redox reactions in waterbody sediments, thus is not bio-available. Lanthanum can only be extracted from rhabdophane in the laboratory using strong acid extraction methods.

Laboratory studies with Phoslock demonstrated that no lanthanum released within 24 hours when granular Phoslock (10 mg/L) was dissolved in de-ionized water; and only a small concentration of lanthanum (~0.016 mg/L or 3% of the total lanthanum in Phoslock) was released from the 10 mg/L concentration of Phoslock when dissolved in low alkalinity natural water or synthetic soft water (*Yasseri and Nowak 2008*).

Even if the total amount of lanthanum applied to a system following a Phoslock application became readily available in water (which it does not due to the Phoslock formulation and the fact that lanthanum binds to phosphates in water), the margin of safety associated with lanthanum toxicity is very high. For example, free lanthanum levels following an application dose of 75 mg/L Phoslock in Barensee Lake, Germany resulted in a peak level of 0.130 mg La^{+3}/L shortly after application and <0.02 mg/L one month later. Toxicity tests from this Barensee Lake project revealed an EC_{50} of 103 mg La^{+3}/L zooplankton (*Daphnia magna*) and EC_{50} of 150 mg La^{+3}/L for fish eggs (*Danio rerio*). The peak level of La^{+3} detected in the lake following application was approximately 800 and 1,150 times lower than the EC_{50} concentrations for zooplankton and fish eggs respectively.

The main potential for free lanthanum in water following a Phoslock application is in waters that have a very low alkalinity (< 20 mg/L) and low phosphate concentration (<0.005 mg/L). Typical Phoslock applications are not conducted in waters with low alkalinity and low phosphate levels. Even in these low alkalinity aquatic environments, the concentration of dissolved lanthanum associated with the product is very low and below predicted toxicity thresholds. In these systems, risks can be further mitigated by several other assessment and management strategies such as conducting pre-application laboratory "jar tests" using lake water and lowering and/or splitting the Phoslock dose over time through a series of applications. Due to the ability of organisms to readily process lanthanum (through the liver) and the low level of free lanthanum that potentially becomes available for a short period of time following Phoslock applications, the aquatic toxicity risk and hazard to aquatic organisms is negligible.† While free lanthanum can be used in tests to assess the toxicity to organisms, lanthanum in Phoslock, or bound as rhabdophane, is not free and unlikely to become available or achieve concentrations of toxicological concern in the natural aquatic environment.

Exposure to water column biota

The phosphorus removal capacity of Phoslock does not change drastically under different chemical or environmental conditions. From a water chemistry standpoint, the binding and removal of Phoslock is a straight forward process. Phoslock binds to phosphates over a pH range of 4 to 11, and binds to phosphates under aerobic and anaerobic conditions. Water analysis during and after application reveals no significant change in pH and no need to buffer treated waters during or after a Phoslock application. A pH change in the water column, sediment water interface and bottom sediments will not result in a release of lanthanum from Phoslock and phosphorus bound as rhabdophane. Since Phoslock rapidly settles to the sediments, the potential exposure duration to organisms in the water column is relatively short. Also, due to the unique formulation of Phoslock, the lanthanum remains sorbed to the clay until it is displaced by phosphates, and subsequently only disassociates a minimal amount of free lanthanum to the water.

Invertebrates

Data were compiled from numerous different testing agencies on a range of sentinel water column invertebrates. Responses of these zooplankton species, including both mortality and reproduction, were evaluated throughout Phoslock exposures. The data show a wide margin of safety associated with Phoslock (*Table 1*) applications at predicted use rates and environmentally relevant concentrations.

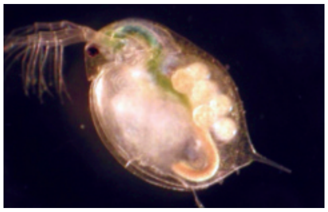


Table 1. Description of Phoslock toxicity experiments with sentinel zooplankton species.

Species	Endpoint	Test Duration	Lowest Observed Effect Concentration (LOEC)*	Water	Reference
Ceriodaphnia dubia	Mortality	48 hours	> 50mg/L Phoslock	Field water	Ecotox 2008
Ceriodaphnia dubia	Reproduction	7 days	> 1mg/L Phoslock	Field water	Ecotox 2008
Ceriodaphnia dubia	Mortality	7 days	> 1mg/L Phoslock	Field water	Ecotox 2008
Ceriodaphnia dubia	Mortality	48 hours	> 12,500 mg/L Phoslock	Synthetic soft	Stauber, 2000
Daphnia magna	Mortality	48 hours	> 50,000 mg/L Phoslock	Synthetic soft	Martin & Hickey, 2004

** Due to the amount of Phoslock needed to result in impacts to biota, many studies did not test concentrations high enough to result in significant impacts, thus toxicity endpoints are reported as greater than the highest concentration tested and does not indicate the actual lowest observed effect levels.*

Fish

The responses of numerous fish species to Phoslock exposures has been evaluated to determine potential risks following application. No mortality or adverse impacts to fish have been observed in field applications in the United States or internationally. Based on data generated for several different fish species (*Table 2*), there is minimal risks to fish expected with applications of Phoslock at standard dose rates in aquatic environments.

Table 2. Description of Phoslock toxicity experiments with sentinel fish species.

Species	Endpoint	Test Duration	Lowest Observed Effect Concentration (LOEC)*	Water	Reference
Melanotaenia duboulayi	Mortality	96 hours	> 50,000 mg/L Phoslock	Synthetic soft	Ecotox 2006a
Oncorhynchus mykiss	Mortality	96 hours	> 3,125 mg/L Phoslock	Synthetic soft	Martin & Hickey, 2004
Oncorhynchus mykiss	Mortality	48 hours	> 13,000 mg/L Phoslock	Natural pond-field	Watson-Leung 2008

** Due to the amount of Phoslock needed to see impacts to biota, many studies did not test concentrations high enough to result in significant results, thus toxicity endpoints are reported as greater than the highest concentration tested and does not indicate the actual lowest observed effect levels.*

Exposure to benthic organisms

When Phoslock settles at the sediment-water interface it forms a thin (< 2 mm) permeable layer that continues to actively bind phosphate released from the sediments or that from inflow. Due to the fine particulate nature of Phoslock, it does not produce a thick flocculent layer at the sediment-water interface. When the lanthanum in Phoslock binds to phosphate, the resulting mineral complex $LaPO_4$ is formed. This stable mineral has a very low water solubility co-efficient ($K_{sp} < 10^{-27}$) and is not bio-available to benthic organisms. Lanthanum is a naturally occurring earth element found in soils throughout the United States (Shacklette H.T, Boerngen J.G, 1984). A soil study conducted by the University of California detected lanthanum at an average background level of 20.3 mg La/kg in soil samples collected throughout California (Kearney, 1996). Concentrations in waterbody sediments, prior to any Phoslock application, have been measured from 8 to 37 mg/kg dry weight on average and many European river sediments have up to 44 mg/kg dry weight (Yasseri and Nowak, 2008). Background levels of lanthanum (bound in forms with chlorides, carbonates and phosphates) in water bodies sediments tested globally (US, Europe and Australia) have typically ranged from 12 - 36 mg La/kg, with occasional extreme exceptions high and low (Phoslock Water Solutions, 2011).

During and after Phoslock application, the additional lanthanum to the waterbody's sediment is negligible. As a result of typical variation in background sediment concentrations, Phoslock applications are not expected to provide a significant or quantifiable change in total Lanthanum concentration in the bottom sediments of treated waterbodies.

Table 3. Description of Phoslock toxicity experiments with benthic invertebrates.

Species	Endpoint	Test Duration	Lowest Observed Effect Concentration (LOEC)*	Water	Reference
Chironomus zealandicus	Mortality & emergence & sex ratio	38 days	All > 400mg/L Phoslock	Lake water	Clearwater 2004
Chironomus dilutus	Mortality	10 days	> 3,400mg/L Phoslock	Pond water	Watson-Leung, 2009
Polypedilum parvidum	Mortality	10 days	> 400mg/L Phoslock	Field water	Clearwater & Hickey 2004
Hyalella azteca	Survival and growth	14 days	> 450mg/L Phoslock	Pond water	Watson-Leung, 2009
Hexagenia **sp.**	Survival and growth	21 days	> 450mg/L Phoslock	Pond water	Watson-Leung, 2009
Macrobrachium **sp. (shrimp)**	Mortality	96 hours	> 50,000 mg/L Phoslock	Synthetic soft water	Ecotox, 2006b
Macrobrachium **sp.**	Mortality	7 days	> 800 mg/L Phoslock	Synthetic soft water	Ecotox, 2006b
Macrobrachium **sp.**	Mortality	14 days	> 800 mg/L Phoslock	Synthetic soft water	Ecotox, 2006b

** Due to the amount of Phoslock needed to result in impact biota, many studies did not test concentrations high enough to significant impacts, thus toxicity endpoints are reported in the greater than the highest concentration tested and does not indicate the actual lowest observed effect levels.*

A variety of different benthic invertebrates have been evaluated in toxicity experiments to determine potential risks associated with Phoslock applications. Responses variables in these studies included survival, emergence time, growth and sex ratio at emergence. Even with long exposure durations and high Phoslock concentrations, no significant impacts were observed with benthic organisms at and above predicted use rates. The predicted risk is negligible and no field toxicity has been observed.

Phoslock and Human Health

There is a very low potential exposure to lanthanum in Phoslock after being applied due to the minimal bio-availability. Even if an exposure occurs, lanthanum is readily processed by the liver and excreted with no negative impacts observed. Lanthanum is used in a prescription drug called Fosrenol® to decrease blood phosphate levels in humans. The Food and Drug Administration approved human dose rate for Fosrenol is 750 to 3,000 mg/day.

Exposure via Ingestion of Treated Water

In case of lanthanum ingestion via drinking even a large volume of Phoslock treated reservoir water, there is negligible risk to human health. Applying Phoslock on a reservoir at the dose rate of 50 ppm (a typical dose rate of Phoslock in a waterbody with an average concentration of phosphorus and alkalinity) and assuming that 100% of La (5% La in Phoslock) was released out of the product (which does not happen because alkalinity and PO4 will bind the "free" La in surface waters), the person would need to drink 80 gallons of reservoir water per day to ingest the minimum dose that corresponds to the lowest Fosrenol daily intake. Drinking 2 gallons of water daily under these artificial conditions would result in consuming La levels 40 times lower than the minimum daily dose of Fosrenol. The maximum dose of Fosrenol is 3,000 mg/day; the average person would need to drink 317 gallons of reservoir water per day to receive the maximum dose of La that is the Fosrenol daily intake. These large volumes of water could not be consumed by a person per day. Drinking Phoslock treated water directly after an application would pose negligible risk to human health.

Exposure via Fish Consumption

The risk via consuming Phoslock/lanthanum in fish harvested from Phoslock treated water after application was negligible as shown in a fish health investigation, after three successive applications of Phoslock in Lake Okareka, New Zealand. The Lake Okareka fish health monitoring report (*Landman et al., 2007*) demonstrated that trout and koura accumulated lanthanum only in the liver and hepatopancreas tissues, not in the flesh/muscle following the application of Phoslock. It was also demonstrated that lanthanum was removed from the fish liver and hepatopancreas tissues within a few months and the concentrations of lanthanum returned to baseline before another Phoslock application one year later, suggesting a biological capacity to depurate lanthanum (*Landman et al., 2007*). This is also consistent with the findings that the main excretion route for absorbed lanthanum in humans or animals is via the liver into bile (*Damment & Pennick, 2007*). The highest concentration of lanthanum measured in the liver of male and female trout in Lake Okareka after one and two months of Phoslock application was 1.2 and 0.8 mg/kg. Similarly, the highest concentration of lanthanum in the hepatopancreas tissues of male and female trout was 0.8 and 1.0 mg/kg respectively (*Landman et al., 2007*). Therefore, in total the highest concentration of lanthanum in one trout was 2.0 mg/kg. Thus, a person would need to consume 826 pounds of fish per day to ingest the minimum dose of La that corresponds to the lowest Fosrenol daily intake. The average person would need to consume 3,306 pounds of fish per day to consume the maximum daily dose of La from Fosrenol. These large quantities of fish would not be consumed by a person per day. If a person consumed 2 pounds of fish this would result in consuming La levels 400 times lower than the minimum daily dose of Fosrenol. Moreover, fish liver and hepatopancreas tissues are not generally consumed by humans. Even consumption of large quantities of fish liver and hepatopancreas tissues harvested from Phoslock treated waterbody would pose negligible risk to human health.

Lanthanum is not a Hazardous Substance

Phoslock is not considered hazardous by the Occupational Health and Safety Administration (OSHA) Hazard Communication Standard (*29 CFF 12910.1200*). Lanthanum and the clay used in the formulation are not listed on the USEPA Toxic Substances Control Act inventory list. Lanthanum is not on the Australian National Occupational Health and Safety Commission (OHSC) List of Designated Hazardous Substances (*NOHSC, 1999a*).

No risk has been associated with contact of Phoslock. The main potential for human exposure to Phoslock is during the application process. Due to some small particulates in the formulation, there could be some potential eye irritation and inhalation for applicators and handlers associated with an application. Applicators and handlers should follow suggested personal protective equipment guidelines found on the package label and material safety data sheet.

Summary

Phoslock is patented phosphorus locking technology that has been specifically formulated to decrease potential exposure to aquatic biota. Phoslock poses a negligible to very low risk to the aquatic environment while providing a high affinity to bind and remove phosphorus that results in improvements to water quality. A review of toxicity data has shown a large margin of safety to aquatic organisms and humans that may be exposed to Phoslock treated water during and following application.

Phoslock phosphorus locking technology is NSF/ANSI Standard 60 certified for use in drinking water. This certification ensures that Phoslock applications, at the maximum use rate specified on the product label, does not contribute contaminants that could cause adverse human health effects. NSF/ANSI Standard 60 is the nationally recognized health effects standard for products which are used to treat drinking water.
In addition, this certification requires annual product testing, facility inspections, quality assurance, good manufacturing practices, and product stock inspections. The United States Environmental Protection Agency and all states rely on and accept ANSI accreditations by authorized independent third party accreditation agencies, such as Water Quality Association (WQA).

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SePRO Corporation
11550 North Meridian Street
Suite 600
Carmel, IN 46032 U.S.A.
317.580.8282
800.419.7779

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

Line Dithmer [a, b], Ulla Gro Nielsen [a], Miquel Lürling [c], Bryan M. Spears [d], Said Yasseri [e], Daniel Lundberg [f], Alanna Moore [d], Nicholai D. Jensen [a], Kasper Reitzel [b, *]

[a] Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark
[b] Department of Biology, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark
[c] Aquatic Ecology & Water Quality Management Group, Department of Environmental Sciences, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands
[d] Centre for Ecology & Hydrology, Penicuik, Midlothian, Scotland EH26 0QB, UK
[e] Institut Dr. Nowak, Mayenbrook 1, D-28870 Ottersberg, Germany
[f] Department of Chemistry and Biotechnology, Swedish University of Agricultural Sciences, P.O. Box 7015, SE-750 07 Uppsala, Sweden

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ABSTRACT

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

1. Introduction

Eutrophication of freshwaters is a global problem caused mainly by elevated phosphorus (P) concentrations in the sediment due to P emissions from agriculture and sewage. Control and regulation of these emissions have improved significantly in recent years, in order to fulfil legislation on water quality, such as the European Water Framework Directive (European Union, 2000). However, the release of legacy stores of P in lake bed sediments can confound catchment management by maintaining elevated water column TP concentrations for decades and may also need to be controlled. Chemical lake restoration, also referred to as geo-engineering, has been demonstrated as a measure for controlling sediment P release resulting in rapid chemical recovery following catchment management (Mackay et al., 2014; Spears et al., 2014). To date, chemicals including iron (Fe) and aluminium (Al) in the form of oxides and hydroxides have been widely used for P control in lakes (Boers et al., 1992; Cooke et al., 1993; Welch and Schrieve, 1994; Welch and Cooke, 1999; Lewandowski et al., 2003; Reitzel et al., 2005) but engineered materials like the lanthanum-modified bentonite Phoslock® (LMB) (Douglas et al., 1999; 2002; Copetti et al., this issue) have received increasing attention in recent years. Most published literature on LMB has focused on laboratory or mesocosm studies (Egemose et al., 2010; Reitzel et al., 2012, 2013; Bishop et al., 2014; Lürling et al., 2014), with assessment of chemical and

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* Corresponding author.
E-mail address: reitzel@biology.sdu.dk (K. Reitzel).

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

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

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

2. Methods and materials

2.1. Study sites and sample collection

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

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

Table 1

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

Lake	Place	Date	Additional treatments	Area (ha)	Depth mean (m)	Alk (mmol L^{-1})	DOC (mg L^{-1})	TP$_{pre}$ (μg L^{-1})	TP$_{post}$ (μg L^{-1})	Chl. A.$_{pre}$ (μg L^{-1})	Chl. A.$_{post}$ (μg L^{-1})
Otterstedter See	DE	nov-06	Hypolimnetic withdrawl	4.5	5.0	0.8	9.6	59[1]	35(2)[11]	n/a	n/a
Silbersee	DE	nov-06	Hypolimnetic withdrawl[+]	7.0	5.0	1.6	4.3	150[2]	158(4)[11]	n/a	n/a
Rauwbraken	NL	mar-08	Flocculent (PAC)[a,b]	2.6	8.8	0.4	4.7	133(143)[3]	15 (13)1[12]	28 (85)[3]	4 (6)[12]
H. G. Eiland	NL	apr-08		5.0	2.5	2.0	2.8	32 (26)[4]	29 (26)[13]	n/a	n/a
Kuil	NL	apr-09	Flocculent ($FeCl_3$)*	6.7	4.0	2.8	9.2	72 (126)[5]	12 (6)[14]	22 (28)[5]	5 (3)[14]
Blankensee	DE	dec-09		22.5	1.6	0.8	8.6	10[6]	n/a	38[6]	n/a
Behlendorfer See	DE	dec-09	None*	64.0	6.2	1.6	9.3	110[7]	n/a	26[7]	n/a
Eichbaumsee	DE	nov-10	Flocculent (PAC)[b]	23.2	6.5	2.5	5.9	358[8]	91[15]	32[8]	28[18]
Mere Mere[c]	UK	mar-13		15.8	2.8	1.3	14.4	77[16]	75[17]	16[16]	13[17]
Hatchmere[c]	UK	mar-13		4.7	1.4	2.0	16.7	83[16]	73[17]	18[16]	32[17]

[a] Lürling and van Oosterhout (2013a, b).

[b] PAC (polyaluminumchloride).

[c] Spears et al. (2013a).

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

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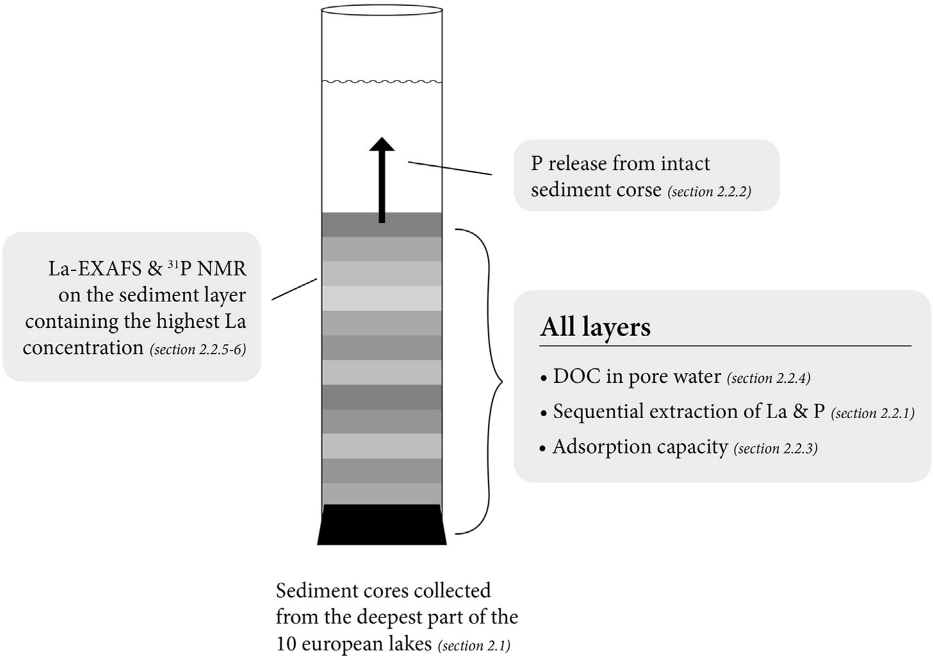

Fig. 1. Overview of the analysis performed on the sediment cores from the ten lakes.

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

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

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

2.2. Sediment analysis

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

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

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

2.2.2. SRP flux experiments on intact sediment cores

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

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

2.2.3. *SRP adsorption experiments*

The SRP binding capacity of each sediment layer was determined by suspending 1 g fresh sediment ($n = 3$) from each layer of the pooled sediment (from four cores, see section 2.1) in 40 mL purified water containing 1.98 mg L^{-1} SRP added as K_2HPO_4, with pH adjusted to 6.5 using NaOH. Soluble reactive P concentrations were measured before and after incubation for approx. 24 h on a shaking table, followed by separation of sediment and solution by centrifugation (10 min, RCF = 1200), filtration of the supernatant (cellulose acetate membrane filter 0.45 μm) and acidification of the filtrate (2 M sulphuric acid).

2.2.4. *Pore water analysis*

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

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

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

2.2.6. *L_{III}-EXAFS*

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

In all spectra, double electron excitations were observed, an anomalous feature common in EXAFS for lanthanides (Solera et al., 1995; Ohta et al., 2008). This was removed with built-in functions in EXAFSPAK (George and Pickering, 2000). In addition, the Barium (Ba) L_{II}-edge (at 5624 eV) was observed. This interference is caused by the Ba content in the LMB (620 μg Ba g^{-1} DW (Spears et al., 2013b)), naturally occurring Ba in the bed sediments (e.g. 5–600 μg Ba g^{-1} DW in Clatto Reservoir, UK (Meis et al., 2012)) or both. A pre-treatment sediment sample from Loch Flemington, UK, was used as reference to counteract for this interference, by performing a baseline subtraction of a linearly scaled background measurement with a strong Ba L_{II} peak, effectively removing the interfering Ba peak without affecting the rest of the data set. Data treatment was performed in EXAFSPAK and afterwards fitted with scattering paths obtained with FEFF 7.02 (Zabinsky et al., 1995). The data were analysed using refinement of single-scattering La-O distances, and the distances for pure synthesized rhabdophane ($LaPO_4 \cdot H_2O$) is 2.47(1) Å and for monazite ($LaPO_4$) 2.52(1) Å (Dithmer et al., 2015a) were used as initial distances. Additional scattering pathways (La–P, La–O–P, La–C, La–O–C) were included with fixed average distances determined from ICDD and FEFF-calculations, and not refined due to the complexity of the EXAFS data.

2.3. *Statistical analyses*

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

3. Results

3.1. *Vertical distribution of La and P in the sediment*

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

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

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

3.2. *Depth dependent sediment adsorption capacity*

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

3.3. *SRP flux experiments on intact sediment cores*

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

3.4. *Pore water analysis*

Pore water DOC concentrations in Lake Het Groene Eiland were below 6 mg DOC L^{-1} for all sediment layers, whereas concentrations in Lake Otterstedter See, Hatchmere, and Lake Rauwbraken were all above 15 mg L^{-1}, with the remaining six lakes ranging between 5 and 15 mg L^{-1} (Fig. 4).

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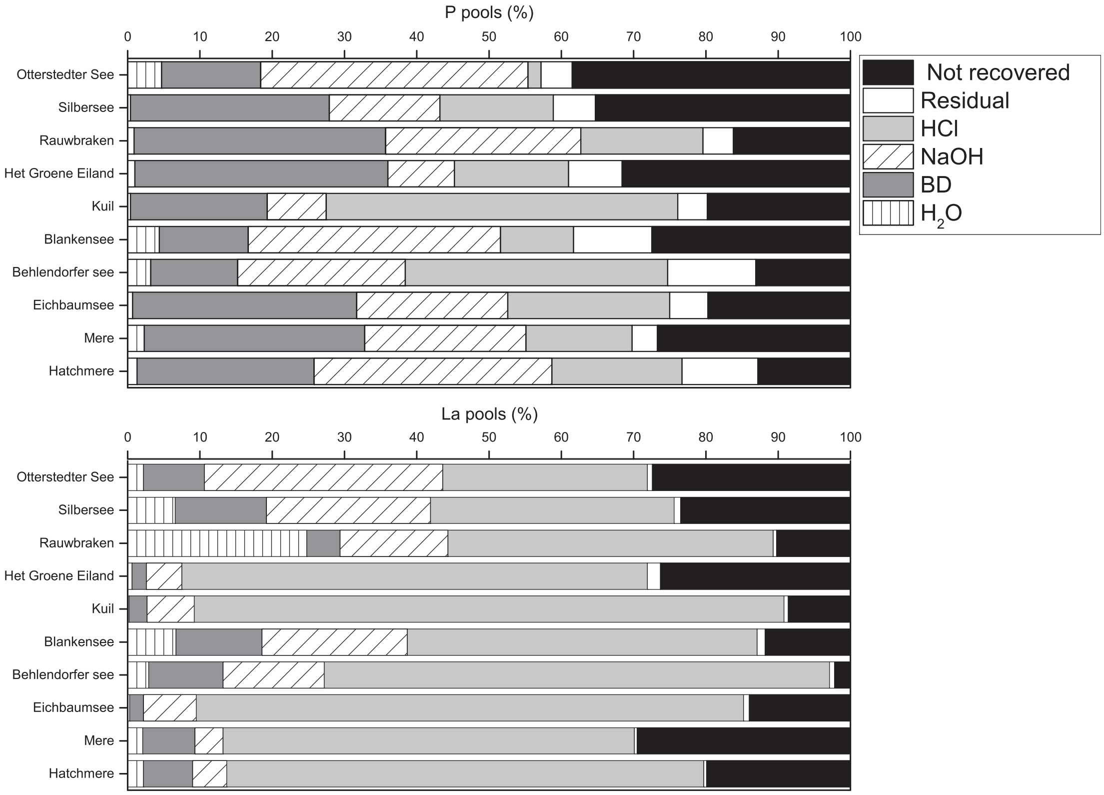

Fig. 2. The distribution (%) of TLa and TP in the various accumulated (upper 10 cm) fractions from a sequential extraction: H_2O-, BD-, NaOH-, HCl-, residual and the un-recovered fractions.

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

3.5.1. ^{31}P MAS NMR spectroscopy

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

3.5.2. La L_{III}-EXAFS

The sediment samples from the ^{31}P NMR study were also analysed by EXAFS (Table 5). The bond-distances, $d_{La\text{-}O}$, were determined from extracted k^3-weighted $X(k)$ functions and the corresponding Fourier Transforms (Figure SI-2). The distances were assigned to be representative for rhabdophane, except in Lake Behlendorfer See (2.51(1) Å) and Lake Blankensee 2.56(1) Å), which were assigned to either monazite or a mixture of rhabdophane, monazite and unreacted La in the clay matrix, as previously observed by Dithmer et al. (2015a). The La concentrations in sediment samples from Lakes Silbersee and Het Groene Eiland were too low for a reliable analysis of the EXAFS data.

4. Discussion

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

4.1. Speciation of La and P in the sediment

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

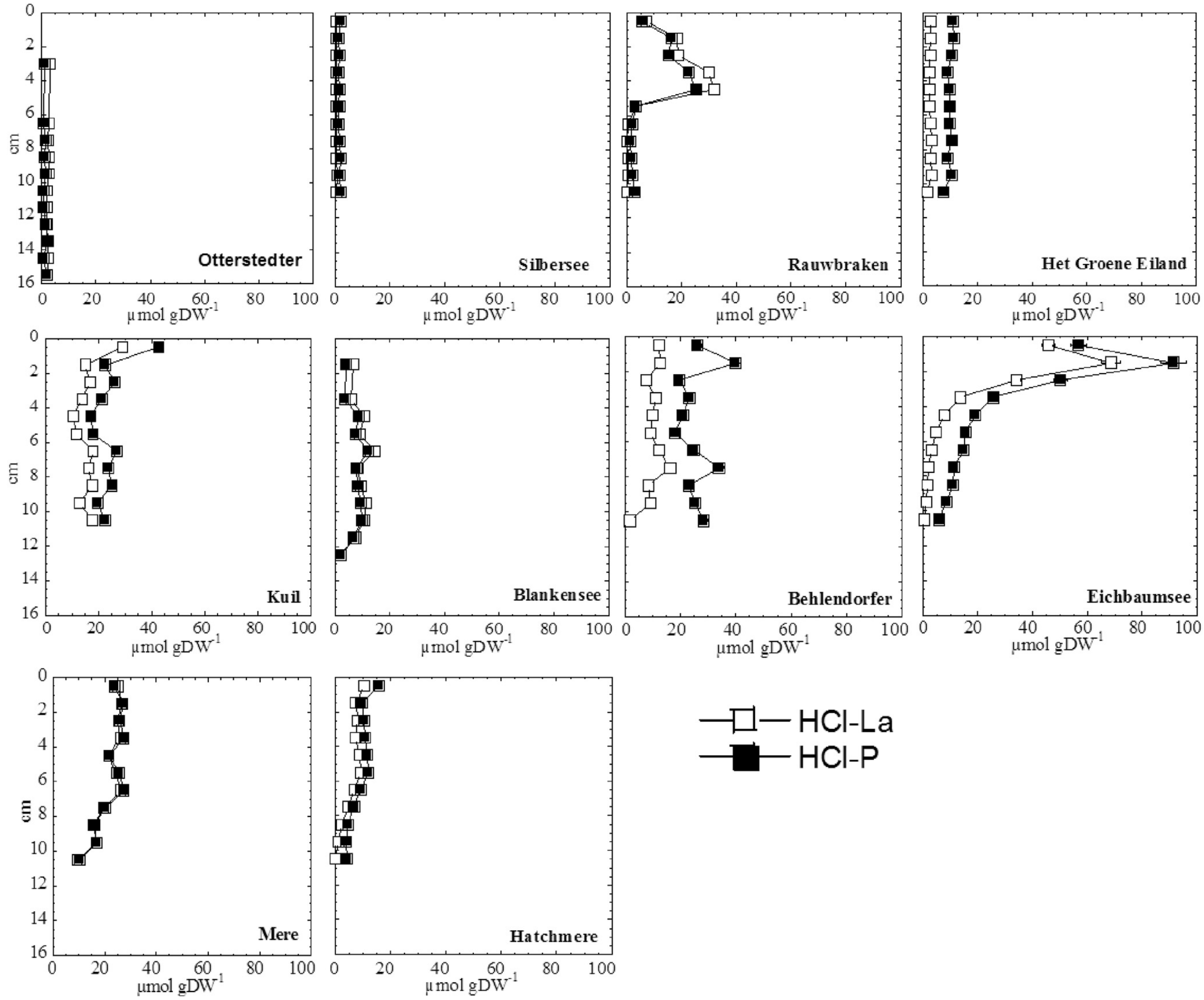

Fig. 3. The HCl-extractable content of La (white) and P (black) in the sediment profile of the ten LMB treated lakes.

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

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

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

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

4.2. Vertical distribution of La in the sediment

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

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

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

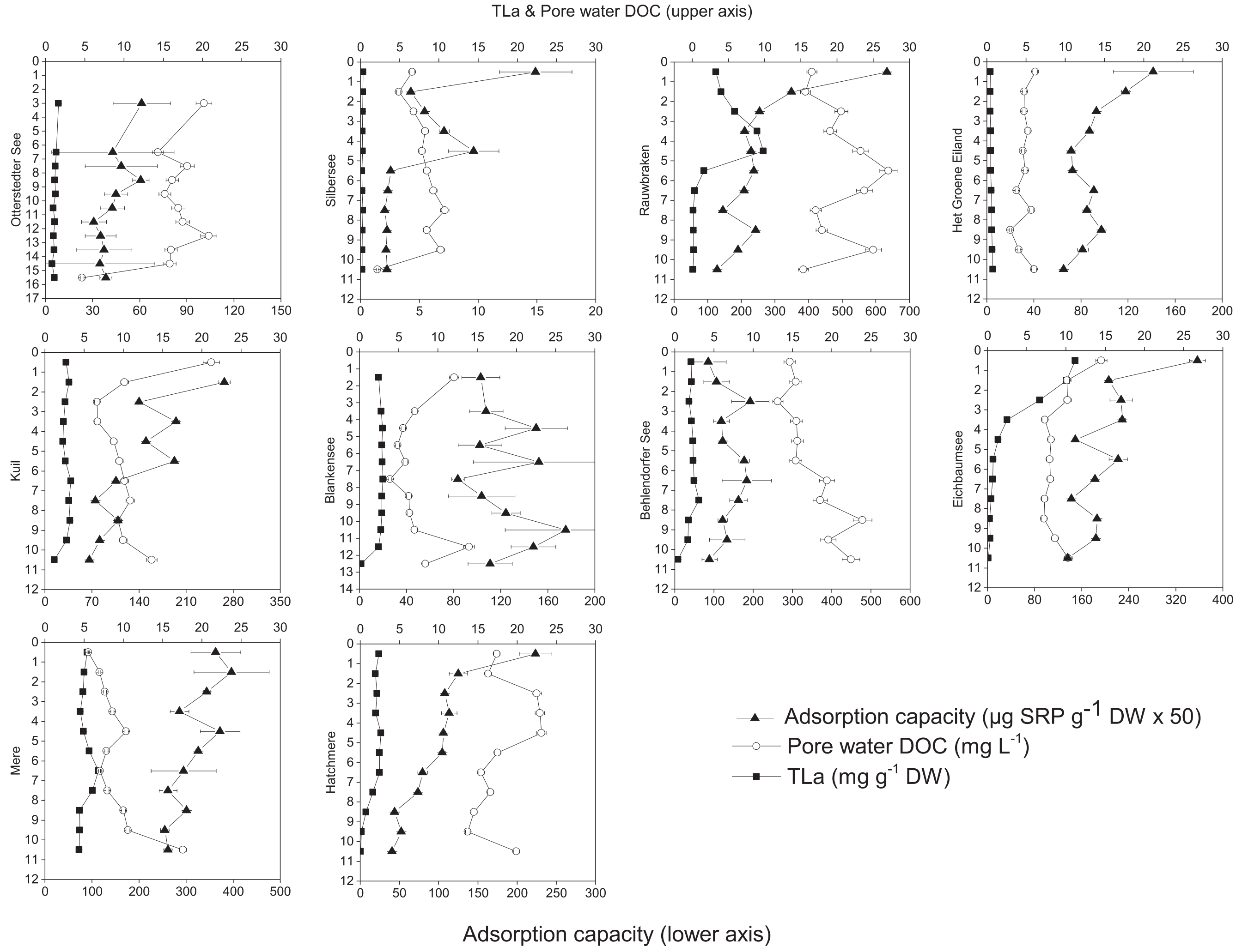

Fig. 4. Total La content and pore water DOC concentration (upper axis) and adsorption capacity (lower axis) in the sediment profile for ten lakes. Note different scales on the lower x-axis (adsorption capacity).

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

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

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

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

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

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

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

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

4.3. Molar La:P ratio in the sediment

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

A high DOC concentration has been reported to retard LMB P-binding processes (Lürling and Faassen, 2012; Reitzel et al., 2013; Lürling et al., 2014; Dithmer et al., this issue), and DOC concentrations in the pore waters of five of the six lakes with HCl extractable La:P > 1 (Lake Otterstedter See, Lake Rauwbraken, Lake Behlendorfer See, Hatchmere, and Lake Blankensee) were high in relation to the above studies (10 mg L^{-1}, threshold value according to Lürling et al., 2014). Further evidence of the complication of La and DOC lies within the slightly longer La–O bond distances in the 'high DOC' lakes (Lake Rauwbraken, Lake Blankensee, Lake Behlendorfer See, and Hatchmere) compared with 'low DOC lakes', which indicates association of La with DOC within the clay (Dithmer et al., 2015a). The apparent role of DOC in confounding LMB performance in the sediments is also in agreement with the results from 16 Danish lakes, where the SRP binding capacity in the lake water was found to be negatively correlated with DOC in a seven day laboratory experiment (Dithmer et al. (this issue)), and it was found that high alkalinity may counteract the negative influence of high DOC on adsorption capacity. This could explain the high La:P ratio and low SRP adsorption capacities discussed above for Lake Otterstedter See, and to some extent for Lake Rauwbraken, which had high concentrations of pore water DOC and low surface water alkalinity. In the current study, the SRP adsorption capacity was evaluated by 24 h incubations, and the immobilization of SRP within LMB may take longer than this experimental period. Dithmer et al. (this issue) demonstrated that the apparent reduction of LMB P binding capacity in the presence of DOC can be overcome by simply increasing the incubation time; i.e. the P binding capacity is not necessarily lower, but, instead, the rate of uptake is slower.

4.4. Evidence of SRP release from the sediment

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

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

Rhabdophane ($LaPO_4 \cdot n\ H_2O$) is a stable mineral, but can eventually condense thermodynamically into the even more stable monazite ($LaPO_4$) (Dithmer et al., this issue). Rhabdophane was identified as the main La phosphate mineral in nine of the ten lakes. In Lake Otterstedter See, the dominant La phosphate mineral identified by ^{31}P NMR was monazite. This finding is in agreement with Dithmer et al. (this issue) who demonstrated that aging of rhabdophane can lead to the formation of monazite. Lake Otterstedter See was the lake first treated (2006) of our ten lakes which may explain this result. Lake Silbersee was treated at the same time, but has had multiple LMB treatments subsequently, which might have influenced the ^{31}P NMR analysis as well as the EXAFS analysis, so a mixture of "older" and "newer" La phosphate minerals is apparent in the sediments of this lake. Given this explanation, one would expect a gradient of mineral formation with sediment depth.

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

4.6. Perspective

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

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

5. Conclusions

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

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Appendix A. Supplementary data

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

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Operational Evaluation of Phoslock Phosphorus Locking Technology in Laguna Niguel Lake, California

West M. Bishop · Terry McNabb · Ian Cormican · Ben E. Willis · Shaun Hyde

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Abstract Management strategies that prevent the onset of nuisance and noxious cyanobacteria blooms are needed to preserve the integrity and safety of freshwater resource uses. Scientifically defensible data are needed regarding efficacy of proactive approaches in order to assist water resource managers in making informed decisions. As phosphorus availability has been indicated as a crucial aspect of cyanobacteria presence/dominance in freshwater systems, the integration of novel technologies to inactivate phosphorus is a critical component to achieve improved water quality. Phoslock (Phoslock Water Solutions, Ltd.) phosphorus locking technology is composed of the element lanthanum in a bentonite clay matrix that has a high specificity to bind and inactivate soluble reactive phosphorus. This research evaluated the phosphorus binding efficiency of Phoslock in aqueous and sediment matrices and the consequent impact on algae assemblage composition and water quality parameters. Laguna Niguel Lake in California afforded an opportunity to evaluate the operational effectiveness of Phoslock in a system historically plagued by high phosphorus concentrations, potentially toxic cyanobacteria (*Aphanizomenonflos-aquae* dominant), and lake closures. Phoslock was able to rapidly (<2 weeks) and significantly ($p<0.0005$) decrease total (>80 %) and free reactive (>95 %) phosphorus in the water column and shift potentially releasable sediment phosphorus fractions to residual forms after treatment. Despite documented cyanobacteria blooms and high pretreatment cell densities, cyanobacteria levels remained below or near detection limits and only comprised a small fraction of the algae assemblage following Phoslock application. This study provides water resource managers an information on operational implementation and efficacy of a phosphorus binding technology.

Keywords Phosphorus · Cyanobacteria · In situ management · Water quality

1 Introduction

As the culprit of numerous human and animal health concerns, cyanobacteria harmful algal blooms (CHAB) have garnered significant attention in management research (Chorus and Bartram 1999; Briand et al. 2003). Approaches to management have included both proactive and reactive. Proactive management is of particular interest due to the identification of crucial environmental factors governing presence and dominance of numerous CHAB. Additionally, abating the presence of CHAB decreases risks of cyanotoxin exposure as well

W. M. Bishop · B. E. Willis (✉)
SePRO Research and Technology Campus, 16013 Watson Seed Farm Road, Whitakers, NC 27891, USA
e-mail: ben.willis@sepro.com

T. McNabb · I. Cormican
AquaTechnex, LLC, 2124 Grant Street, Bellingham, WA 98225, USA

S. Hyde
SePRO Corporation, 11550 N. Meridian Street, Carmel, IN 46032, USA

as offsets the need for reactive (e.g., pesticide) solutions, which have recently experienced increased regulatory scrutiny (USEPA 2011). Field validation is needed to support the efficiency and efficacy of proactive management approaches. This research provides water resource managers with scientifically defensible data on a strategic solution to address phosphorus pollution, a key supporting factor of CHAB.

Phosphorus has been indicated as an environmental pollutant of concern especially in terms of accumulation in freshwater resources and correlation with CHAB (Carpenter 2008; Schindler 2012). Phosphorus concentrations and the relationship between nitrogen and phosphorus (N/P ratio) can govern the presence and intensity of CHAB (Smith 1983; Seale et al. 1987; Paerl 1990; Paerl et al. 1991; Ghadouani et al. 2003). To impact the long-term water quality and algae assemblage, addressing phosphorus availability is critical. Water resources can accumulate significant amounts of phosphorus from a variety of sources (e.g., watershed, atmospheric, and point source discharges). The ability of some planktonic cyanobacteria to regulate buoyancy allows rapid uptake and storage of hypolimnetic phosphorus even when epilimnetic phosphorus is limiting (Ganf and Oliver 1982; Kromkamp et al. 1989).

Sediments can act as a sink or source for phosphorus depending on numerous environmental conditions (e.g., pH, dissolved oxygen, conductivity; Nürnberg 1997; Søndergaard et al. 2003; Schindler 2012). Sequential phosphorus extractions are required to accurately assess the mobility of phosphorus in sediments in relation to forms potentially viable for assimilation by CHAB (Jansson et al. 1988; Pettersson and Istvanovics 1988; Gonsiorczyk et al. 1998; Dignum et al. 2004). Internal cycling of historically accumulated phosphorus needs to be addressed as water quality improvement may be significantly delayed with only decreases in watershed phosphorus inputs (Jeppesen et al. 2005; Welch and Cooke 2005; Mehner et al. 2008; Spears et al. 2012). Evaluation of management strategies that rapidly and preferentially bind aqueous phosphorus as well as alter sediment-associated phosphorus toward less mobile forms is critical in freshwater management.

Phoslock is a patented lanthanum-modified bentonite clay formulation designed to inactivate available phosphorus in water and sediments (Douglass 2002). Phoslock was developed by the Commonwealth Scientific and Industrial Research Organization (CSIRO) of Australia to promote phosphorus uptake in surface water resources while decreasing risks from dissolved lanthanum to aquatic biota. The lanthanum-phosphate complex is highly insoluble, stable under differing environmental conditions, and can form with low concentrations of reactants over a wide range of pH levels (Firsching and Brune 1991; Diatloff et al. 1993; Haghseresht et al. 2009). Preliminary field scale applications of Phoslock have resulted in significant decreases in water column phosphorus concentrations and decreases in cyanobacterial presence (Robb et al. 2003). Additional research by Meis et al. (2012) documented decreases in potentially mobile sediment phosphorus fractions (i.e., labile, reductant-soluble) and concomitant increase in the most tightly bound fractions (i.e., apatite/residual). As in situ phosphorus mitigating technologies are limited, and in acknowledgment of the nontarget species safety (Watson-Leung 2009) and binding specificity (Reitzel et al. 2013) of Phoslock, it is critical to understand the applicability to combat eutrophication in freshwaters and the consequent ability to proactively alter algae assemblage composition.

By understanding the ability of phosphorus mitigating technologies to inactivate bioavailable phosphorus and resultant implications for the water resource, effective proactive strategies can be implemented to support management objectives and achieve compliance standards. The overall purpose of this research was to evaluate the potential of a novel phosphorus mitigating technology to promote desired water resource integrity. Specific objectives of this research were to (1) measure the change in free reactive phosphorus (FRP) and total phosphorus (TP) concentrations in the water column following Phoslock application to a hypereutrophic water resource, (2) assess the benthic macroinvertebrate community in upstream and downstream areas pre- and post-Phoslock application, (3) measure the impact of Phoslock amendments on sediment phosphorus fractions, and (4) compare the pretreatment algal assemblage and water quality conditions to those of posttreatment conditions.

1.1 Study Site

Laguna Niguel Lake (Sulfur Creek Reservoir) has a surface area of 12.42 ha with a 3.66-m average depth (9.45-m max depth) and is located between Laguna Niguel and Aliso Viejo, California, in Orange County (33° 32′ 50″ N; 117° 42′ 20″ W). The watershed is primarily composed of residential neighborhoods with storm water runoff contributing to external nutrient loadings, although few residents live directly on the lake. One major tributary (Sulfur Creek) feeds Laguna Niguel Lake draining a catchment area of 16 km^2. The lake was built in 1966 with the construction of Sulfur Creek Dam which is the source of a spillway for constant outflow. The primary beneficial uses are as a scenic recreation location for the public, a waterfowl sanctuary, and local fishing resource. Complaints of poor appearance, green color, surface algae blooms (cyanobacteria), odor, declining fishery, outbreaks of avian botulism and overall low esthetic quality spurred the need for management.

2 Materials and Methods

2.1 Sample Collection and Analysis

Water samples were collected periodically from three locations throughout reservoir. Samples were collected in 2012 and for 2 months leading up to the Phoslock application to attain background water quality conditions. Water quality parameters were measured according to standard methods which included pH, dissolved oxygen, temperature, alkalinity, chlorophyll *a*, Secchi depth, total nitrogen, turbidity, and algae assemblage composition and densities (SMEWW 2005). Aqueous and sediment-associated lanthanum concentrations were also measured 4 days after completion of the Phoslock application at four locations throughout the lake and upstream and downstream of the system (USEPA method 6020). TP and FRP were measured colorimetrically on a discrete analyzer (Konelab Aqua 420) according to standard methods (USEPA 1978). Benthic macroinvertebrate sampling and assessment were conducted both upstream and downstream of the lake immediately before treatment (April 29, 2013) and 4 days after Phoslock application completion (May 6, 2013) in accordance with NPDES permit compliance monitoring (Fig. 1). Procedures followed the Surface Water Ambient Monitoring Program (SWAMP) protocols with sorting/taxonomy conducted according to standard methods by Aquatic Bioassay Laboratories, Inc. in Ventura, California (Richards and Rogers 2006; Ode 2007).

Sediments were collected using an AMS threaded stainless steel coring apparatus pretreatment (April 29, 2013), 3- and 6-month posttreatment (August 7, 2013, December 4, 2013). The top 8-cm layer of sediment was analyzed to discern the influence of Phoslock on phosphorus fractions in the lake sediments (Meis et al. 2012), for each of the three sites in the lake. Site 2 was excluded from the 3-month posttreatment sampling event due to similarities between sites 1 and 2 pretreatment analyses ($p<0.05$). Composite sediment samples were placed in polyethylene centrifuge tubes, filled completely to minimize air space, stored in the dark at <4 °C for transport to the SePRO Research and Technology Campus (Whitakers, NC) for processing. Sequential extraction was used to determine relevant phosphorus fractions and compare concentrations of bioavailable and residual forms following Phoslock treatment. Procedures incorporated methods modified from Chang and Jackson (1957), Psenner (1988), Meis et al. (2012), and Kapanen (2008) and included the following: (1) extraction in 1 M NH_4Cl (100 mL) for 30 min to determine loosely adsorbed P (labile P), (2) extraction with 0.11 M $NaHCO_3$/0.11 M $Na_2S_2O_4$ (100 mL) for 1 h terminated by removal of supernatant to determine P mainly bound to Fe-hydroxides or manganese (Mn) compounds (reductant-soluble P), (3) extraction with 0.1 M NaOH (100 mL) for 16 h to release hydroxide exchangeable (soluble reactive phosphorus, metal oxide bound P; TP, soluble reactive phosphorus, organic P), and (4) persulfate acid digestion to calculate apatite and residual bound P (Table 1).

2.2 Phoslock Application

The amount of Phoslock necessary to inactivate phosphorus in this system was calculated based on a 1:1 molar ratio of La/P (100 kg Phoslock/1 kg phosphorus) calculated on the TP measured in the water column and potentially releasable phosphorus in sediments (labile, reductant-soluble, metal oxide). A total of 51.34 MT of Phoslock was added to this system to target water measured aqueous and releasable sediment phosphorus by first mixing into slurry in tanks on each boat. Application encompassed a 4-day period (April 29, 2013 to May 2, 2013), and GPS tracking was used to ensure accurate distribution across the water body surface at a designated volume per acre coverage. Phoslock was distributed heterogeneously across four established treatment zones based on surface area, water depth,

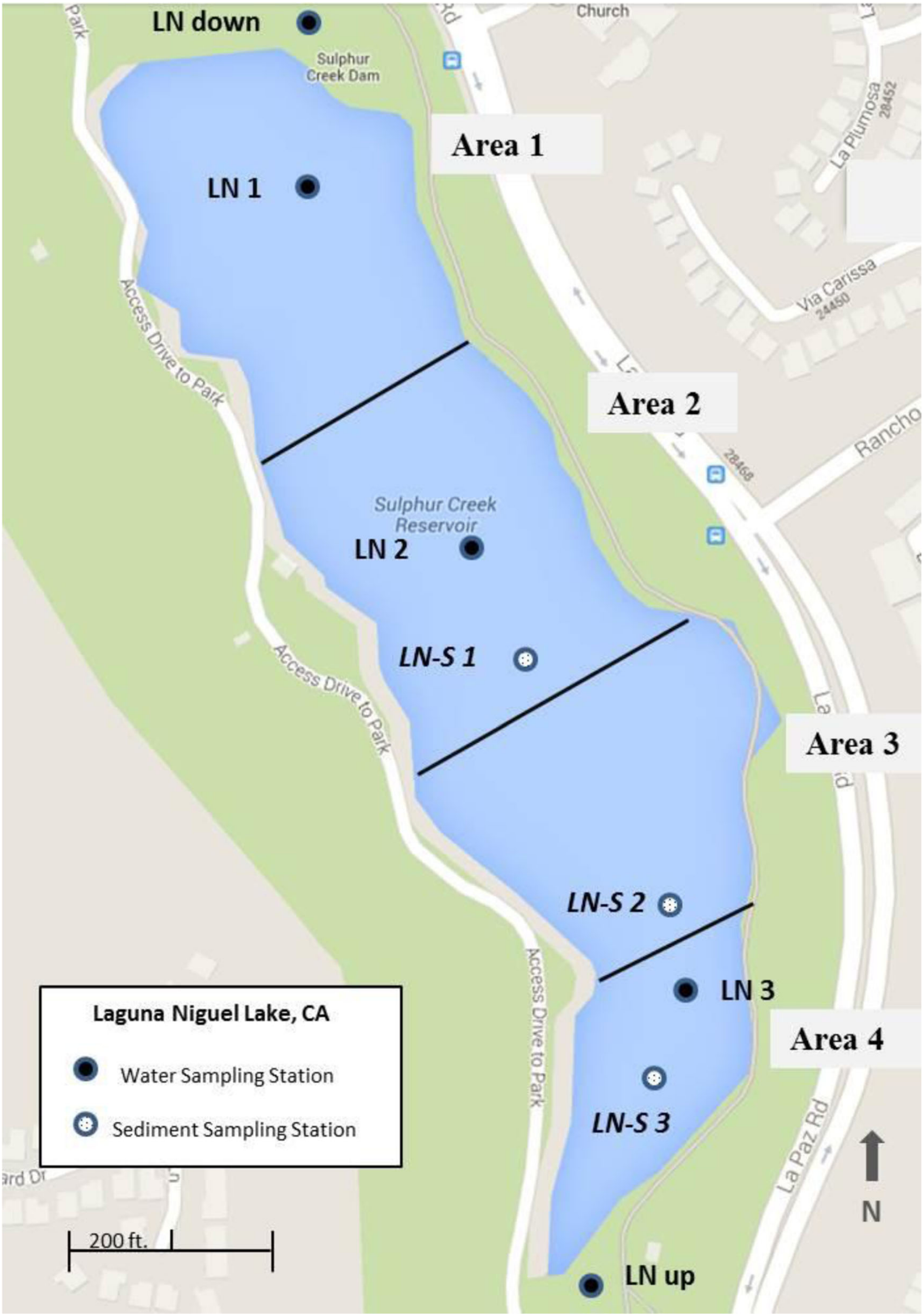


Fig. 1 Map of Laguna Niguel Lake and designation of water and sediment sampling locations and depiction of treatment areas

Table 1 Description of sediment phosphorus fractions from sequential extraction procedures

Phosphorus fraction	Description of phosphorus fraction	Release mechanisms	Relative bioavailability	References
'Labile P'	Directly available P; pore water P; loosely bound or adsorbed P	Desorption; diffusion; concentration gradients	High	Boström et al. (1988); Hupfer et al. (1995); Spears et al. (2007)
'Reductant-soluble P'	P bound to Fe-hydroxides and Mn-compounds	Anoxia, low redox	High	Psenner et al. (1988); Boström et al. (1988); Hupfer et al. (1995); Lukkari et al. (2007); Spears et al. (2007)
'Metal-oxide adsorbed P'	P adsorbed to metal oxides (mainly Al, Fe); P exchangeable against OH	pH (e.g., photosynthetic activity)	Medium/high	Psenner et al. (1988); Boström et al. (1988); Hupfer et al. (1995); Lukkari et al. (2007)
'Organic P'	Biogenic P	Biodegradation	Medium/high	Psenner et al. (1988); Boström et al. (1988); Hupfer et al. (1995); Lukkari et al. (2007); Meis et al. 2012
'Apatite bound P'/ 'Residual P'	P bound to carbonates and apatite minerals; refractory compounds	Low pH strong digestion	Low	Psenner et al. (1988); Boström et al. (1988); Hupfer et al. (1995); Spears et al. (2007)

sediment characteristics, and total amount of phosphorus targeted (Fig. 1, Table 2).

2.3 Statistical Analysis

An ANOVA was used to assess differences in response parameters between means of sampling events through time and coupled with pairwise multiple range testing (Holm-Sidak method) to distinguish significance ($p<0.05$). Data were assessed for normality using a Shapiro-Wilk test as well as for equal variance. Differences in sediment phosphorus fractions before and after Phoslock application were discerned with paired Student's *t* test ($p<0.05$). All data were analyzed using Microsoft Excel® 2007 and SigmaPlot® 12.1.

3 Results

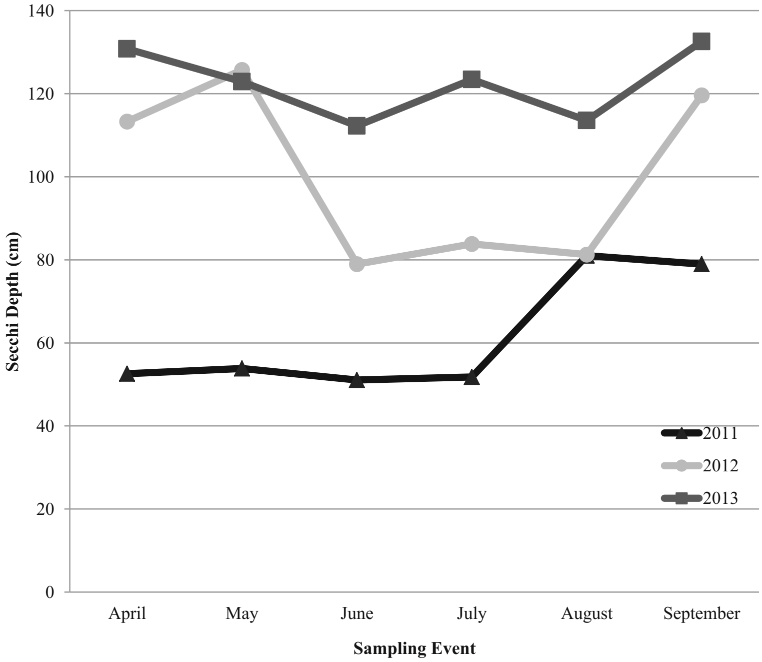
3.1 Water Quality and Biota Analyses

Water quality parameters remained consistent and at acceptable levels in Laguna Niguel Lake throughout the study with ranges of pH (7.1–8.3 SU), turbidity (0.8–6.7 NTU), conductivity (2.55–3.19 mS), dissolved oxygen (7–11 mg/L), and alkalinity (158–199 mg/L as $CaCO_3$). Aqueous lanthanum concentrations were <6 μg/L at all sites monitored (upstream in lake and downstream) 4 days after completing the Phoslock application. Secchi depth greatly increased post-Phoslock application with an average of 122.6 cm from April to September, 2013 compared to corresponding depths of

Table 2 Description of Phoslock application characteristics specific to differing lake zones (Fig. 1)

Treatment area	Total acres (ha)	Average depth (m)	Total Phoslock/area (MT)	Vortex output (kg per min)	Transect spacing (m)	Total distance of transects (m)
1	4.31	5.79	19.06	45.36	6.1	7,070.05
2	3.21	4.57	13.80	45.36	6.1	5,264.37
3	3.22	2.74	12.87	45.36	6.1	5,277.64
4	1.68	1.52	5.61	45.36	6.1	2,761.63
Total	12.42	3.66	51.34	–	–	20, 374

Fig. 2 Secchi depth measurements from April to September over a 3-year period pre- and post-Phoslock application in Laguna Niguel Lake



61.6 and 100.5 cm in 2011 and 2012, respectively (Fig. 2). TP and FRP concentrations from posttreatment sampling events on May 14, 2013, July 17, 2013, and September 4, 2013 were significantly less than pretreatment events of the same year and previous year ($p<0.01$, Fig. 3). Samples from 4-day post-Phoslock application were not significantly different although a substantial rainfall was documented during this

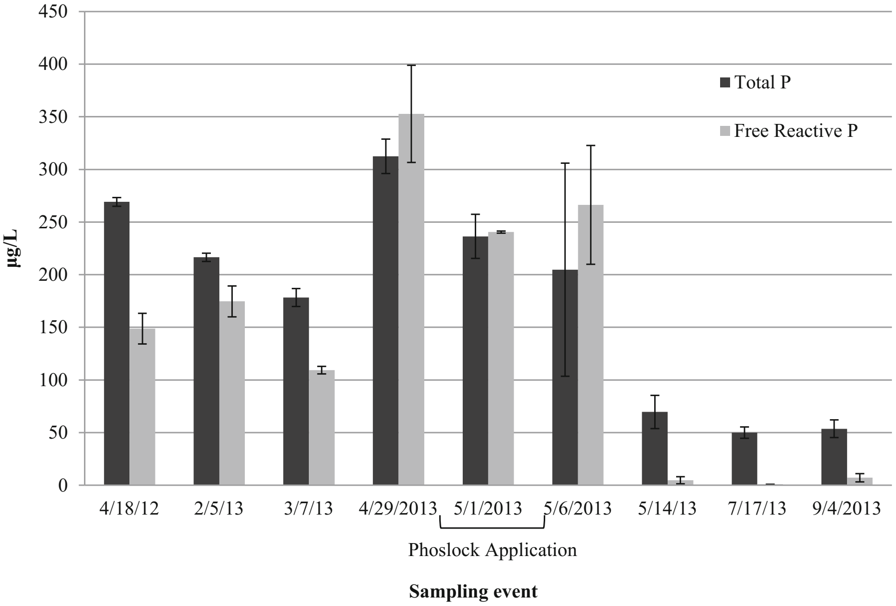


Fig. 3 Total and free reactive phosphorus concentrations from three sampling locations (LN1–3) throughout Laguna Niguel Lake at different sampling events. *Error bars* represent one standard deviation. *Underlined event* represents sampling during the Phoslock application period

sampling event (0.84 cm). The pretreatment algae assemblage was dominated by cyanobacteria (primarily *Aphanizomenon flos-aquae*) with an average density of 33,300 cells/mL whereas posttreatment algae samples contained significantly lower densities of cyanobacteria (average 1,200 cells/mL) with assemblages primarily composed of green algae and diatoms (average 6,000 cells/mL, Fig. 4). In previous years, 10–12 copper-based algicide applications were required on an annual basis to maintain the desired a esthetic quality of the water resource (Ian Cormican, Personal Communication, December 18, 2013). Increased a esthetic quality and no noticeable scum formations were observed post-Phoslock treatment, and no reactive algicide applications were required for cyanobacteria control in 2013.

An increase in aquatic macrophytes (*Ruppia maritime* [Widgeongrass] dominant) was also observed in this system, not seen previously in over a decade, as a likely function of increased light penetration. Invertebrate communities were not significantly impacted following addition of Phoslock based on richness, diversity, and functional feeding groups (Table 3). The habitat score was similar in preapplication and postapplication as measured by the following: in stream cover, sediment deposition, water chemistry, and channel alteration.

3.2 Sediment Phosphorus Composition

Compared with immediate pretreatment levels, sediment phosphorus fractions were significantly different between pretreatment (April 29, 2013) and 3-month posttreatment (August 7, 2013). There were significant reductions of the labile, reductant-soluble, and organic phosphorus fractions and significant increases of the metal-oxide and apatite and residual fractions 3 months after treatment (α=0.05). Significant differences were sustained for the sediment phosphorus fractions 6 months after treatment (December 4, 2013), except with the reductant-soluble fraction which was not significantly different than the pretreatment concentration (α=0.05, Fig. 5).

4 Discussion

Phosphorus levels have been implicated in increased frequency and intensity of CHAB in freshwaters (Carpenter 2008; Schindler et al. 2008). Addressing watershed inputs is important for long-term water quality improvement but may not be adequate by itself to achieve use goals or meet compliance standards. Recycling of legacy phosphorus from lake sediments can be a significant and ongoing phosphorus source

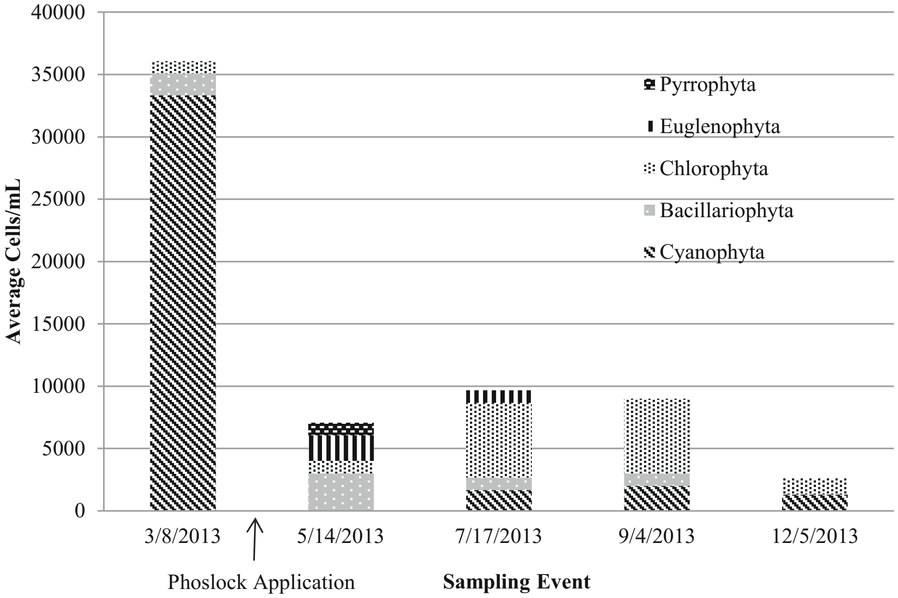


Fig. 4 Algae assemblage composition at different sampling events in Laguna Niguel Lake. Values are averages from three sampling locations (LN1–3). *Arrow* represents Phoslock application

Table 3 Benthic macroinvertebrate biometrics for upstream (LN up) and downstream (LN down) sampling locations pre- and post-Phoslock application

Metric	Pre-event		Post-event	
	LN-down	LN-up	LN-down	LN-up
Richness measures				
Taxonomic richness	7	8	9	12
EPT taxa	0	0	0	0
Coleoptera taxa	0	0	0	0
Predator taxa	1	2	2	3
Composition measures				
EPT index (%)	0	0	0	0
Sensitive EPT index (%)	0	0	0	0
Shannon diversity	0.84	0.68	0.66	1.33
Percent dominant taxa	70.7	80	81.8	54.6
Percent noninsect individuals	93.9	91	97	80.9
Percent noninsect taxa	71.4	50	44.4	41.7
Tolerance/intolerance measures				
Percent Hydropsychidae	0	0	0	0
Percent Baetidae	0	0	0	0
Mean tolerance value	7.8	7.8	7.9	7.4
Percent intolerant individuals (0–2)	0	0	0	0
Percent tolerant individuals (8–10)	92.4	90.7	94.9	74.2
Percent tolerant taxa	42.9	25	44.4	41.7
Percent Chironomidae	5.8	8.1	2.4	16.4
Functional feeding groups				
Percent collectors and filterers	98.5	99.5	99.2	98.1
Percent collectors	98.2	99.2	99	98.1
Percent filterers	0.3	0.3	0.2	0
Percent scrapers	0.2	0	0	0.5
Percent shredders	0	0	0	0

(Søndergaard et al. 2003; Welch and Cooke 2005). Therefore, addressing the direct and immediate in situ loading as well as external sources is necessary for effective water resource management. The impacts of phosphorus may not manifest until present in water bodies via loss of instrumental and intrinsic water resource uses from CHAB (recognized by stakeholders) which demands a direct need for management. In this research, Phoslock was measured to specifically inactivate and maintain low levels of soluble reactive phosphorus while not altering pH and alkalinity that are important factors to an aquatic ecosystem.

Phoslock has a specific affinity toward phosphorus over a range of environmental conditions allowing a readily calculable amount for designated phosphorus mitigation (Reitzel et al. 2013). The pH values throughout this study were all between 7.1 and 8.3 representing values that should not interfere with lanthanum affinity to phosphorus compounds (Ross et al. 2008). Lanthanum may react with hydroxyl species under high pH conditions (>8.35) and decrease the potential binding efficiency. Haghseresht et al. (2009) found a 29 % decrease in adsorption capacity at pH 9 versus 5 in line with the Ross et al. (2008) findings of decreased adsorption capacity at pH >9. This may have been a function of the decreased exposure time as the settling rate of Phoslock was increased in higher pH waters, likely due to the particulates coagulating as pH increases (Ross et al. 2008). Alternatively, Gibbs et al. (2011) found an increase in binding capacity when pH was increased from 6.1 to 8.9, suggesting that pH impacts may differ by water body.

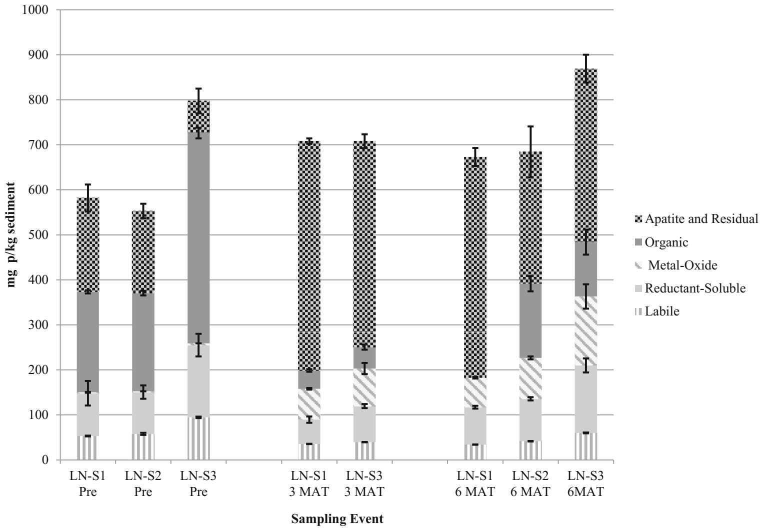


Fig. 5 Sediment phosphorus fractions in Laguna Niguel Lake from pre-Phoslock application as well as 3 and 6 months after treatment (MAT). *Error bars* represent 95 % confidence intervals (n=3)

Specific dosing is important in calculating rates necessary to remove targeted phosphorus amounts. Reitzel et al. (2013) found minimal interference at 1.07–1.15 La/P molar binding ratios with Phoslock binding efficiency even in estuarine situations. Other technologies may possess significant interference from water characteristics and sediment composition, which results in large shifts of molar ratios (>100:1) required to remove phosphorus (Rydin and Welch 1999).

Sediment phosphorus can be a significant and ongoing source that fuels CHAB (Søndergaard et al. 2003). Understanding the fate of Phoslock and associated phosphorus and binding integrity is critical for evaluating long-term impacts to water quality. Upon interacting with free phosphorus forms, Phoslock forms a highly stable mineral (e.g., rhabdophane; $LaPO_4{\cdot}nH_2O$) that is expected to remain bound with conditions common in water resources (Ross et al. 2008). Phoslock was able to significantly shift potential releasable phosphorus forms to apatite and residual forms in Laguna Niguel Lake, which maintained throughout the duration of this study. This was similarly measured by Meis et al. (2012) who found a shift in Clatto Reservoir sediments to refractory compounds and 79 % of Phoslock bound phosphorus to not be release sensitive after 28 days in laboratory experimentation. Sediment-associated lanthanum did increase above background in Laguna Niguel Lake (742-mg/kg DW posttreatment vs 27-mg/kg pretreatment) as expected as Phoslock is designed to incorporate with sediments. This was also documented from Meis et al. (2012), who found significant increases in sediment lanthanum content (mg/kg DW) down through 8 cm of sediment corresponding with amount of Phoslock applied.

Nontarget species safety is critical in maintaining the ecological integrity of a system following treatment to mitigate phosphorus. Lanthanum in Phoslock is adsorbed to a bentonite clay matrix through a patented cation exchange process. This was found to enhance the uptake and removal of free phosphorus while decreasing potential for dissolved lanthanum in the receiving aquatic system (Haghseresht et al. 2009). The retention of La in the bentonite matrix decreases the potential exposure to nontarget species, therefore reducing risks. Similar to Lurling and Tolman (2010), little dissolved lanthanum was detected in water posttreatment with ~0.001 % of the applied concentration being detected in water of Laguna Niguel Lake 4 days after completing application. Laboratory toxicological bioassays have documented chronic lowest observed effect levels of Phoslock for benthic macroinvertebrates at >400 mg Phoslock/L (Clearwater 2004; Clearwater and Hickey 2004; Watson-Leung 2009). Results of this study further support the ecological safety associated with Phoslock exposures as no significant composition or diversity alteration was measured posttreatment with the benthic macroinvertebrate community via upstream and downstream comparison. This is a field validation of predicted laboratory toxicity thresholds as the potential Phoslock exposure in Laguna Niguel Lake was approximately 112 mg Phoslock/L, assuming an immediate and homogenous application. Based on the design of Phoslock and laboratory/field toxicological and analytical analyses, the predicted exposure concentration and duration necessary to elicit adverse impacts to aquatic biota are unlikely to be achieved with expected use patterns.

In this study, there was a significant and notable desired shift of the algal assemblage from cyanobacteria dominance to green algae and diatoms following phosphorus mitigation with Phoslock. Robb et al. (2003) found a substantial shift away from cyanobacteria blooms in the Vasse River (Australia), though less evident in the Canning River likely due to macrophyte cycling interference. Despite numerous published articles on the effectiveness of Phoslock in phosphorus mitigation (Reitzel et al. 2013; Spears et al. 2012), further correlation was needed on impacts to the algal assemblage composition and preservation of water resource uses.

This research evaluated effectiveness and subsequent impact of a specific phosphorus mitigating technology (Phoslock) through one growing season. Scientifically defensible data are needed to assess the impact of proactive management approaches especially in terms of ability to mitigate the intensity and frequency of CHAB with the recognized global increase and threat to human and animal health (Hallegraeff 1993). In this research, Phoslock was able to significantly decrease and maintain lower concentrations of phosphorus in the water column as well as shift sediment phosphorus fractions to less bioavailable forms compared to pretreatment concentrations. Consequently, the algal assemblage shifted from historic cyanobacteria-dominated blooms at nuisance densities to green algae and diatoms dominant with decreased cyanobacteria presence. Phoslock provides water resource managers an ecologically sound in situ solution to specifically address phosphorus pollution (a key causative factor of CHAB) and an ability to proactively combat this growing affliction to our freshwater resources.

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Lake responses following lanthanum-modified bentonite clay (Phoslock®) application: An analysis of water column lanthanum data from 16 case study lakes

Bryan M. Spears[a,*], *Miquel Lürling*[b,c], *Said Yasseri*[d],
Ana T. Castro-Castellon[e,1], *Max Gibbs*[f], *Sebastian Meis*[a],
Claire McDonald[a], *John McIntosh*[g], *Darren Sleep*[h], *Frank Van Oosterhout*[b]

[a] *Centre for Ecology & Hydrology, Penicuik, Midlothian EH26 0QB, UK*
[b] *Aquatic Ecology and Water Quality Management Group, Department of Environmental Sciences, Wageningen University, PO Box 47, 6700 AA Wageningen, The Netherlands*
[c] *Department of Aquatic Ecology, Netherlands Institute of Ecology (NIOO-KNAW), P.O. Box 50, 6700 AB Wageningen, The Netherlands*
[d] *Institut Dr. Nowak, Mayenbrook 1, D-28870 Ottersberg, Germany*
[e] *Wessex Water, Claverton Down, Bath BA2 7WW, UK*
[f] *National Institute of Water & Atmospheric Research, PO Box 11-115, Hillcrest, Hamilton, New Zealand*
[g] *83A Taneatua Rd, RD 1, Whakatane 3191, New Zealand*
[h] *Centre for Ecology & Hydrology Lancaster, Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster LA1 4AP, UK*

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ABSTRACT

Phoslock® is a lanthanum (La) modified bentonite clay that is being increasingly used as a geo-engineering tool for the control of legacy phosphorus (P) release from lake bed sediments to overlying waters. This study investigates the potential for negative ecological impacts from elevated La concentrations associated with the use of Phoslock® across 16 case study lakes. Impact-recovery trajectories associated with total lanthanum (TLa) and filterable La (FLa) concentrations in surface and bottom waters were quantified over a period of up to 60 months following Phoslock® application. Both surface and bottom water TLa and FLa concentrations were <0.001 mg L^{-1} in all lakes prior to the application of Phoslock®. The effects of Phoslock® application were evident in the post-application maximum TLa and FLa concentrations reported for surface waters between 0.026 mg L^{-1}–2.30 mg L^{-1} and 0.002 mg L^{-1} to 0.14 mg L^{-1}, respectively. Results of generalised additive modelling indicated that recovery trajectories for TLa and FLa in surface and bottom waters in lakes were represented by 2nd order decay relationships, with time, and that recovery reached an end-point between 3 and 12 months post-application. Recovery in bottom water was slower (11–12 months) than surface waters (3–8 months), most probably as a result of variation in physicochemical conditions of the receiving waters and associated effects on product settling rates and processes relating to the disturbance of bed sediments. CHEAQS PRO modelling was also undertaken on 11 of the treated lakes in order

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[*] *Corresponding author*. Tel.: +44 (0)131 445 4343; fax: +44 (0)131 445 3943.
E-mail address: spear@ceh.ac.uk (B.M. Spears).
[1] Current address: Engineering Science Department, University of Oxford, LMH, Norham Gardens, OX2 6QA, UK.

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to predict concentrations of La^{3+} ions and the potential for negative ecological impacts. This modelling indicated that the concentrations of La^{3+} ions will be very low (<0.0004 mg L^{-1}) in lakes of moderately low to high alkalinity (>0.8 mEq L^{-1}), but higher (up to 0.12 mg L^{-1}) in lakes characterised by very low alkalinity. The effects of elevated La^{3+} concentrations following Phoslock® applications in lakes of very low alkalinity requires further evaluation. The implications for the use of Phoslock® in eutrophication management are discussed.

1. Introduction

When assessing the use of management options for the restoration of impacted ecosystems it is essential that any potential unintentional impacts also be considered (Cullen and Boyd, 2008; Matthews and Turner, 2009; May and Spears, 2012). In lakes, geo-engineering using phosphorus (P) capping materials has been used as a management tool with which legacy P stores in bed sediments can be controlled (Hickey and Gibbs, 2009; Cooke et al., 2005; Spears et al., 2013a,b). These legacy P stores can delay ecological recovery following reductions in catchment P loads for decades (Welch and Cooke, 2005; Søndergaard et al., 2003; Spears et al., 2012). Given that current water quality legislation more commonly provides guidance on deadlines by which water quality improvements must be made (e.g. 2015–2027 for the Water Framework Directive, WFD; EC2000/60/EC), research has focussed on identifying methods (e.g. Phoslock® and other P capping agents; biomanipulation; dredging etc.) for ‘speeding up’ the recovery of lakes following catchment management (Hickey and Gibbs, 2009; Jeppesen et al., 2007; Zhang et al., 2010). Recent evidence suggests that when internal P load and catchment P load reduction measures are applied simultaneously, rapid recovery can be achieved (Van Wichelen et al., 2007; Mehner et al., 2008). To meet this demand, novel products continue to be developed and proposed for use in lakes (Zamparas et al., 2012; Spears et al., 2013a,b). Of increasing concern is the lack of understanding of the potential negative impacts on lake ecology and biogeochemical cycling associated with indirect effects of amendment products in lakes (Welch and Cooke., 2005; Vopel et al., 2008; Hickey and Gibbs, 2009; Egemose et al., 2010).

Phoslock® is a lanthanum (La) modified bentonite clay designed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in the 1990s for the control of oxyanions (including dissolved P (DP)) in waste waters and sediments (US Patent 6350383; Douglas, 2002, 2010). The incorporation of La into a bentonite carrier was deemed necessary to reduce the potential for negative ecological effects associated with the liberation of dissolved La^{3+} as described by Haghseresht et al. (2009). In recent years, Phoslock® has been increasingly used as a geo-engineering tool to control the release of legacy P stores from lake bed sediments to overlying waters (e.g. Robb et al., 2003; Lürling and Faassen, 2012; Lürling and Van Oosterhout, 2012; Meis et al., 2012; Van Oosterhout and Lürling, 2011).

Phoslock® is commonly applied from a barge, as slurry, where it acts to strip dissolved P *en route* through the water column. Once settled onto the bed, the product can enhance the capacity of lake bed sediments to retain P in an inorganic particulate form (Meis et al., 2012) that is not available to phytoplankton, and is stable under reducing conditions and within the pH range 5–9, commonly reported in eutrophic lakes (Douglas et al., 2000; Haghseresht, 2006; Robb et al., 2003; Ross et al., 2008). One common operational assumption is that La is not liberated from the bentonite carrier under natural conditions in lakes and that P incorporation into the bentonite matrix is the dominant mechanism of dissolved P removal from solution. However, little empirical evidence exists within the peer reviewed literature (with the exception of Haghseresht et al., 2009) with which the mechanisms of P removal from solution by Phoslock® may be quantitatively identified, although these details are available within confidential reports (Douglas, 2010). This is not the case for the formation of La–P complexes from dissolved species in solution, the mechanisms of which are relatively well documented in the literature (Firsching and Brune, 1991; Firsching and Kell, 1993; Diatloff et al., 1993).

Although the number of publications in which the control of P and/or algal abundance by Phoslock® has been demonstrated has increased in recent years (i.e. 18 publications since 2002 listed in Web of Science), no comprehensive meta-analysis of case study lakes has been conducted, to date. In addition, concern has been raised recently regarding the potential for release of filterable La (FLa) following Phoslock® application and the potential unintended ecological implications of this release (Stauber and Binet, 2000; Hickey and Gibbs, 2009; Lürling and Tolman, 2010). The speciation of FLa ions is also important when considering ecotoxicological impact and of all FLa species (i.e. La^{3+}, $La(OH)^{2+}$, and $La(OH)^{2+}$) the La^{3+} ion carries the greatest risk of biological effects (Das et al., 1988). The application of large aerial loads of inorganic materials (e.g. Phoslock®) may also have a short term impact on aquatic ecology through a sudden increase in suspended matter concentration (Bilotta and Brazier, 2008; Wagenhoff et al., 2012).

A range of laboratory studies have quantified ecotoxicological thresholds related to both total La (TLa) and FLa on components of the aquatic environment (Table 1). However, variation in methodology makes it difficult to draw inferences from these laboratory based trials to the likely impact on populations of organisms in specific lakes under natural environmental conditions (Lürling and Tolman, 2010). However, this body of work can be used to provide an indicative range of threshold concentrations with which concentrations of FLa and TLa, observed in lakes following Phoslock® applications, can be assessed.

Table 1 – Summary of results from acute toxicity assays for organisms in which the stressor was reported as either half maximal effective concentration (EC50) or no observed effect concentration (NOEC) for filterable lanthanum or Phoslock® concentrations.

Test organism	Reported stressor	EC50 (mg L^{-1})	NOEC (mg L^{-1})	Test duration	Reference
Zooplankton					
Daphnia carinata	FLa	0.04–1.18		48 h	Barry and Meehan, 2000
Daphnia magna	FLa	23		48 h	Sneller et al., 2000
Ceriodaphnia dubia	FLa	5.00	2.60	48 h	Stauber and Binet, 2000
Ceriodaphnia dubia	FLa	0.08		48 h	Stauber, 2000
Daphnia magna	Phoslock®	871–1557	100–500	5 day	Lürling and Tolman, 2010
Daphnia magna	Phoslock®	>50,000		48 h	Martin and Hickey, 2004
Daphnia magna	Phoslock®	4900		48 h	Watson-Leung, 2008
Ceriodaphnia dubia	Phoslock®	>50		48 h	ECOTOX, 2008
Ceriodaphnia dubia	Phoslock®	>1		7 day	ECOTOX, 2008
Brachionus calyciflorus	Phoslock®	154	100	48 h	Van Oosterhout and Lürling, 2012
Fish					
Melanotaenia duboulayi	FLa	<600		96 h	Stauber and Binet, 2000
Onocrhynchus mykiss	Phoslock®	>13,600		48 h	Watson-Leung, 2008
Macroinvertebrates					
Hyelella asteca	Phoslock®	>3400		14 days	Watson-Leung, 2008
Hexagenia sp.	Phoslock®	>450		21 days	Watson-Leung, 2008
Chironomus zealandicus	Phoslock®	>450		38 days	Watson-Leung, 2008
Chironomus zealandicus	Phoslock®	>400	400	38 days	Clearwater, 2004

Here we use data from 16 case study lakes to which Phoslock® has been applied to address the following specific research questions: (1) to what type of lakes has Phoslock® been applied and at what range of doses?; (2) what are the ranges of TLa and FLa in treated lakes following application and are there common recovery trajectories across all lakes?; (3) what were the predicted La^{3+} concentrations in the treated lakes according to CHEAQS PRO modelling following Phoslock® application, (4) do reported FLa and TLa concentrations indicate potential issues when compared to laboratory controlled ecotoxicological test results?; and (5) what are the implications of these results for the use of Phoslock® as a eutrophication management tool in lakes?

2. Methods

2.1. *Data availability and study site descriptions*

The following analyses are founded on the results of a survey of the co-authors designed to gather case study information on lakes to which Phoslock® has been applied. Information on location, maximum fetch, mean depth, maximum depth, surface area, annual mean alkalinity, conductivity and pH in the year following product application and Phoslock® dose procedure was requested for each of the 16 lakes for which TLa, FLa or both TLa and FLa data were available for surface and/or bottom waters (Table 2). Contemporary surface (i.e. within the upper 1 m of the water column) and bottom water (i.e. within 1 m of the lake bed) TLa and FLa concentration data were provided for the peak concentrations reported during the application period and for monthly average concentrations before and after the application period, where available. For some of the lakes it was reported that repeat Phoslock® applications had been conducted (i.e. Lake Silbersee, Lake Baerensee; Lake Eichbaumsee; Niedersachsen Lake and Lake Okareka). Only data following the first application of Phoslock® and prior to the second were considered in the following described analyses.

It should be noted that the general approach of product application in Lake Rauwbraken, Lake De Kuil, Lake Eichbaumsee, Lake Ladillensee and Niedersachsen Lake differed from the other lakes in that the product was applied in combination with a flocculent and pH buffer (Van Goethem, 2010; Van Oosterhout and Lürling, 2011). Moreover, application approaches also varied within this subset of lakes. Ferric chloride was used as a flocculent in Lake De Kuil whereas polyaluminium chloride (PAC) was used in Lake Rauwbraken, Lake Eichbaumsee, Lake Ladillensee and Niedersachsen Lake. Approximately 10% of the total Phoslock® dose was applied to Lake Rauwbraken prior to the application of PAC, the remaining quantity of Phoslock® being added following the completion of the flocculation step.

2.2. *Total and filterable lanthanum analysis*

TLa analysis was conducted using inductively coupled plasma optical emission spectrometry (ICP-OES) for all lakes with the exception of Lake Okareka, Lake De Kuil and Lake Rauwbraken for which inductively coupled plasma mass spectrometry (ICP-MS) was used. FLa analysis was conducted using ICP-MS for all lakes from which data were available, with the exception of Niedersachsen Lake for which ICP-OES was used. Limits of detection reported for ICP-MS ranged between 0.00002 mg L^{-1} and <0.0002 mg L^{-1}, and were <0.002 mg L^{-1} for ICP-OES. To normalise detection limits for data analysis the upper reported detection limit was multiplied by 0.5 (i.e. normalised detection limit of 0.001 mg L^{-1}) and applied across all values for all lakes and analytical methods for which the reported TLa or FLa concentration was below 0.002 mg L^{-1}. All water samples for FLa were filtered, however a range of filter types and sizes were used. The ten German lakes were filtered

Table 2 – Summary of data reported for each of the 16 case study lakes to which Phoslock® has been applied and total lanthanum (TLa) and/or filterable La (FLa) concentration data were available for surface and/or bottom waters in the months before and/or after the application period. In the *Lake Name* column, the analytical methodologies used for the determination of TLa and FLa (as 'TLa','FLa' in superscript; 1 – inductively coupled plasma optical emissions spectrometry (ICP-OES); 2 – inductively coupled plasma mass spectrometry (ICP-MS); 0 – no analysis) are summarised. The availability of data for surface and bottom water are summarised as are the date on which the application began and the mass of Phoslock® applied to each lake. UK – United Kingdom, NL – The Netherlands, G – Germany, NZ – New Zealand. Surface? – are data available for surface waters in this lakes?; Bottom? – are data available for bottom waters in this lake? Y – yes; N – no. The lakes included in the PCA analysis are indicated by '3' in square brackets.

Lake name	Country	S.A.	Mean	Max	Fetch	Sample location (TLa//FLa)		Date and mass	Phoslock® load
		(ha)	Depth (m)	Depth (m)	(km)	Surface?	Bottom?	Applied (tonnes)	(Tonnes ha^{-1}/mg L^{-1})
Clatto Reservoir[1,2]	UK	9.0	2.8	7.0	0.4	Y/Y	N/N	04/03/2009 (24.0)	2.67/96.97
Loch Flemington[1,2]	UK	15.7	1.0	2.5	0.7	Y/Y	N/N	15/03/2010 (25.0)	1.59/159.24
Somerset Reservoir[1,0]	UK	2.2	4.5	9.0	ND	Y/N	Y/N	27/03/2007 (6.6)	3.00/66.67
Lake Rauwbraken[2,2]	NL	4.0	8.8	16.0	0.2	Y/Y	N/N	21/04/2008 (18.0)	4.50/51.43
Lake De Kuil[2,2]	NL	7.0	4.0	10.0	ND	Y/Y	Y/Y	18/05/2009 (41.5)	5.93/148.21
Lake Silbersee[1,0,3]	G	7.0	5.0	9.0	0.3	Y/N	Y/N	08/11/2006 (21.5)	3.07/61.43
Lake Otterstedter See[1,0,3]	G	4.5	5.0	11.0	0.3	Y/N	Y/N	30/10/2006 (11.0)	2.44/48.89
Lake Behlendorfer See[1,0,3]	G	64.0	6.2	16.0	2.0	Y/N	Y/N	02/12/2009 (230.0)	3.59/57.96
Lake Blankensee[1,0,3]	G	22.5	1.6	2.5	0.5	Y/N	N/N	16/11/2009 (66.0)	2.93/183.33
Lake Baerensee[1,0,3]	G	6.0	2.6	3.8	0.1	Y/N	Y/N	11/06/2007 (11.5)	1.92/73.72
Lake Kleiner See[1,0,3]	G	0.9	2.0	5.0	0.2	Y/N	Y/N	25/05/2010 (6.0)	6.67/333.33
Lake Eichbaumsee[1,0,3]	G	23.2	6.5	16.0	0.9	Y/N	Y/N	17/11/2010 (148.0)	6.38/92.14
Lake Ladillensee[1,0,3]	G	1.0	2.1	5.0	0.1	Y/N	Y/N	03/03/2009 (4.7)	4.65/221.43
Lake Völlen[1,0,3]	G	2.0	2.5	5.5	0.1	Y/N	Y/N	19/03/2008 (10.0)	5.00/200.00
Niedersachsen Lake[1,1,3]	G	4.2	2.5	6.0	0.1	Y/Y	Y/Y	19/03/2008 (6.0)	1.43/57.14
Lake Okareka[2,2]	NZ	340.0	20.0	34.0	2.8	Y/Y	Y/Y	16/08/2005 (20.0)	0.06/0.29

using laser drilled 0.45 μm cellulose acetate filters, while water samples from Clatto Reservoir and Loch Flemington were filtered through a Whatman GF/F (i.e. 0.7 μm) filter. Lake De Kuil and Lake Rauwbraken samples were filtered using Whatman GF/C filters with a pore size of 1.2 μm. Lake Okareka samples were filtered using 0.45 μm pore size *DigiFilters* (SCP Science).

Estimates of Phoslock® load during application were made by normalising mass of product applied versus both surface area and water volume, the latter being estimated by multiplying mean depth by surface area. The load estimates reported assume complete mixing of product throughout the water column and that no product applied was subject to loss processes from the water column (e.g. loss to lake bed or surface water outflow).

2.3. *Data processing and quantification of recovery trajectories*

Data were summarised as mean monthly surface and bottom water TLa and FLa concentrations relative to the date of Phoslock® application and pooled to produce meta-data in which the maximum number of replicates within each month was $n = 16$, where data from 16 lakes were available. Ranges (including the reported peak concentrations during the Phoslock® application periods) of maximum and minimum TLa and FLa concentrations in bottom and surface waters for each individual lake were extracted from the data and summarised across all lakes to provide an estimate of the impact (i.e. maximum concentrations) and recovery end-point concentrations (i.e. minimum concentrations) across the 16 lakes.

Recovery in TLa and FLa following a Phoslock® application was assessed across the entire population of lakes and is defined as the point at which no further decrease in concentration could be detected using generalised additive models, GAMs (Hastie and Tibshirani, 1990; Wood, 2006), assuming normal errors. In these models the relationship between the response (TLa and FLa) and the explanatory variables (month relative to the Phoslock® application) is allowed to be a smooth function instead of restricting relationships to be linear. Models were developed not for individual lakes but for the whole 16 lake dataset for TLa and FLa in both surface and bottom waters. All of the models were fitted using the gam function in the mgcv package (1.7–6) (Wood, 2011) of statistical software R version 2.15.1. (R Development Core Team, 2012), which is free software available at http://www.r-project.org. Since the aim of the GAM was to identify relationships between TLa and FLa concentration during the month after Phoslock® application the following modelling strategy was employed. A Gamma error structure (log link function) was used in all models and an autocorrelation structure of AC1 (auto-regressive model of order 1) on month relative to the Phoslock® application was used. The responses were not transformed prior to analyses due to the discussion in Zuur et al. (2009).

Although not directly measured in the case studies, Phoslock® concentration in the receiving waters was inferred from volumetric dose (Table 2). Estimates of Phoslock® concentration in receiving waters was also made using

TLa concentration, based on the assumption that Phoslock® is composed of 5% TLa.

2.4. *Modelling the behaviour of lanthanum during recovery*

As colloidal bentonite particles may pass through the various filter sizes used in this study to varying degrees (Koopmans et al., 2005) it was necessary to combine measurements of FLa with chemical modelling in this study to estimate the speciation of dissolved La. The concentration of La^{3+} ions resulting from the dose of Phoslock® to the water column of 11 of the treated lakes, for which sufficient data were available, was modelled using the Chemical Equilibria in Aquatic Systems (CHEAQS PRO) model (Verweij, 2012). This modelling approach was used to complement the direct measurements of FLa, as FLa concentrations are not a direct measure of La^{3+} ions in this study. The following model parameters were used to predict the La^{3+} concentrations following a Phoslock® application: TLa concentrations were inferred using 5% (w/w) TLa in the original dose of Phoslock® for each site and annual average pH, Ca^{2+} $CO_3{}^{2-}$ concentrations (derived from alkalinity) and phosphate concentrations were provided for the lakes. It should be noted that the maximum predicted La^{3+} concentrations may represent an overestimate as this modelling approach assumes that all La would be freed from the clay matrix and we do not simulate the impact of humic acids and oxyanions other than phosphate and carbonate on La^{3+} ion concentration.

Principal components analysis (PCA) using correlation was used to produce the two synthetic axes that best captured the variation in the data (i.e. minimum and maximum TLa in surface water and bottom water, maximum fetch, mean depth, the period (in months) of post application monitoring, and mean alkalinity in the year following application and product dose). Data for annual mean conductivity and pH following application were not used in the analysis as they co-varied strongly with alkalinity. Similarly, maximum depth co-varied strongly with mean depth and so mean depth only was included in the analysis. Data were available for 10 case study lakes (Table 2) for PCA analysis using the above variables. The PCA analyses were carried out using Minitab statistical software, version 14 (Minitab Ltd., Coventry, UK).

3. Results

3.1. *Responses in total and filterable lanthanum concentrations following Phoslock® application*

The results of the co-author survey indicated that FLa and TLa data were available for 16 lakes to which Phoslock® had been applied (Fig. 1, Table 2).

Both surface and bottom water TLa and FLa concentrations were <0.001 mg L^{-1} in all lakes prior to the application of Phoslock® (Figs. 2 and 3). Surface and bottom water peak TLa concentrations during and in the month following the application of Phoslock® ranged from 0.026 mg L^{-1}–2.300 mg L^{-1}

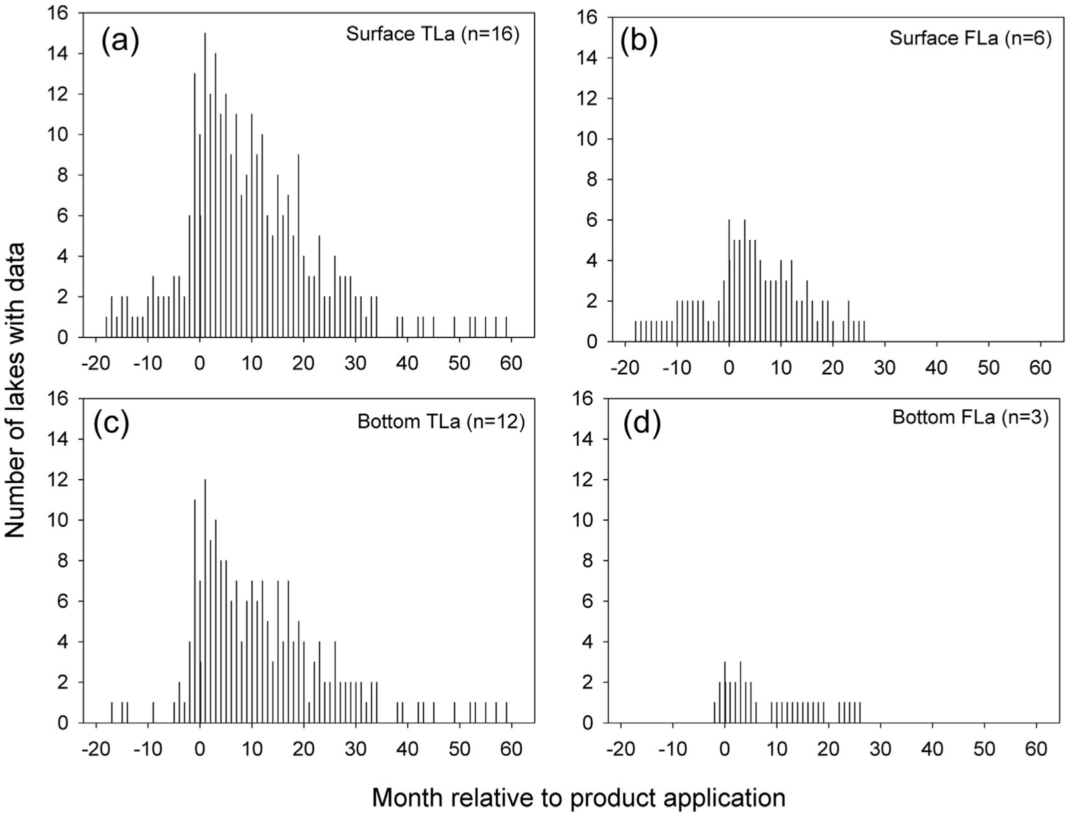

Fig. 1 – Distribution of available data for total lanthanum (TLa; panels a & b) and filterable La (FLa; panels c & d) in surface (panels a & c) and bottom waters (panels b & d) from 16 case study lakes.

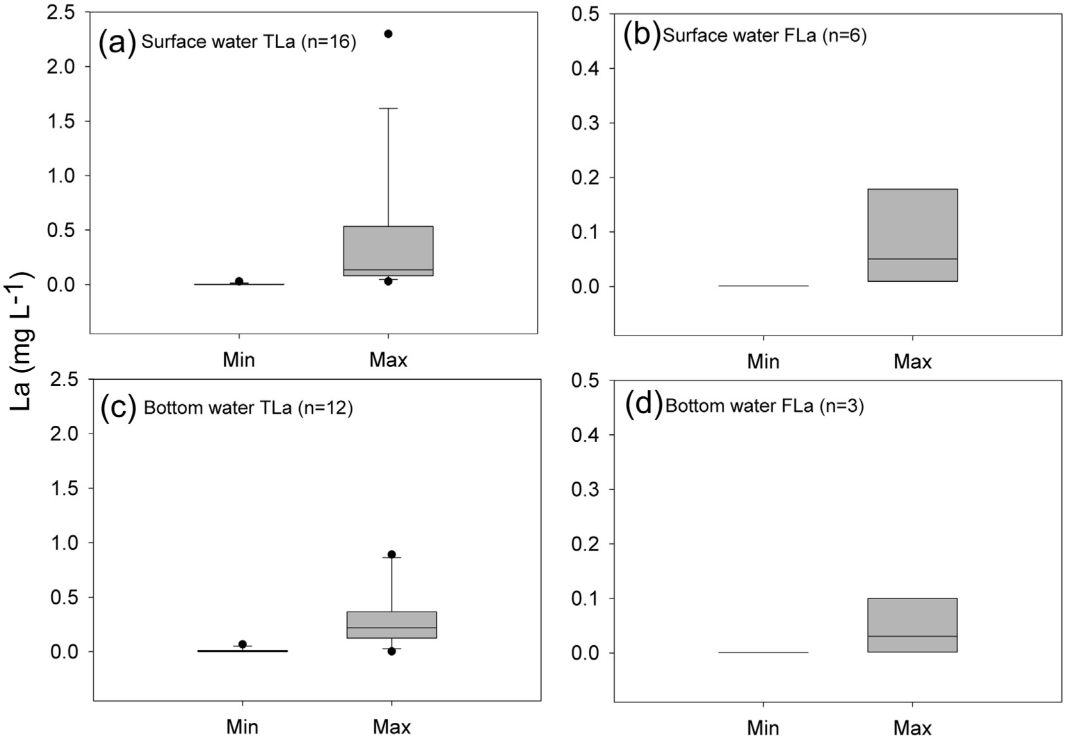

Fig. 2 – Ranges of maximum and minimum total lanthanum (TLa) and filterable La (FLa) concentrations in the months (maximum of 59 months) following an application of Phoslock® to 16 case study lakes. The number of lakes for which maximum and minimum ranges were available is reported in each case. 95th and 5th percentile error bars are shown along with values above or below these values, where appropriate.

and from 0.004 mg L^{-1} to 0.892 mg L^{-1}, respectively. Surface and bottom water peak FLa concentrations following the application of Phoslock® ranged from 0.002 mg L^{-1} to 0.414 mg L^{-1} and from 0.002 mg L^{-1} to 0.100 mg L^{-1}, respectively. Minimum reported values for TLa in surface waters and bottom waters ranged from <0.001 mg L^{-1} to 0.031 mg L^{-1} and from <0.001 mg L^{-1} to 0.068 mg L^{-1}, respectively. However, it should be noted that the values of 0.031 mg L^{-1} and 0.068 mg L^{-1} were reported following only 6 months post-application monitoring in Niedersachsen Lake. Minimum reported values for FLa in surface waters and bottom waters ranged from <0.001 mg L^{-1} to 0.002 mg L^{-1} and were <0.001 mg L^{-1}, respectively.

For the 11 lakes that were included in the CHEAQS PRO model, maximum concentrations of La^{3+} ions following Phoslock® applications were predicted by the model to be below 0.010 mg L^{-1} in ten lakes while one lake was predicted to have a maximum concentration of La^{3+} ions of 0.119 mg L^{-1} (Fig. 4). The concentration of La^{3+} decreased with increasing mean annual alkalinity of the receiving waters following an exponential decay function ($La^{3+} = 404.9629 \times \exp^{(-5.8179 \times \text{Alkalinity})}$, $r^2_{\text{adj}} = 0.999$; $P < 0.001$).

3.2. Quantifying recovery trajectories for total and filterable lanthanum following a Phoslock® application

Results of the GAM are shown in Table 3 and Fig. 5. The 2nd order derivatives of the GAM indicated that there was no further significant decrease in TLa concentration in surface waters following 8 months post-application monitoring and following 11 months for bottom waters. For FLa, GAM results indicated that no further significant decrease was observed following 3 months post-application monitoring in surface waters and 12 months for bottom waters.

3.3. Assessing the drivers of maximum and minimum total lanthanum concentrations following Phoslock® application

The PCA results indicate a general increase in maximum and minimum TLa concentrations in surface and bottom waters along PC 1 (Fig. 6). For surface waters, alkalinity, which was found to be closely correlated with conductivity and pH, varied strongly and negatively with the maximum reported TLa concentration. However, in bottom waters, although alkalinity also appeared to vary negatively with TLa concentration, mean depth and maximum fetch represented stronger, but also negative, co-variants along PC 1. Product dose did not co-vary with maximum or minimum TLa concentration in bottom waters, although weak negative co-variation was apparent between product dose and maximum TLa along PC1 in surface waters. The length of the post application monitoring period did not co-vary strongly with the minimum reported TLa concentrations in either surface or bottom waters.

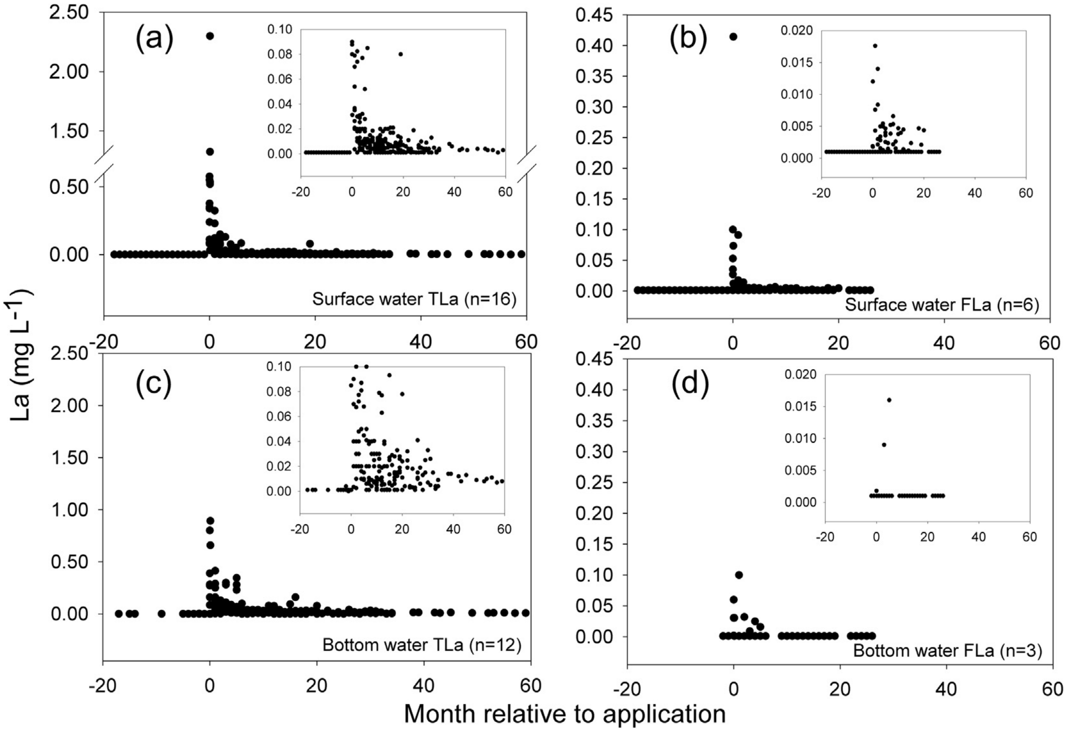

Fig. 3 – Monthly average total lanthanum (TLa; panels a & c) and filterable La (FLa; panels b & d) concentrations in surface (panels a & b) and bottom waters (panels c & d) before and after an application of Phoslock® across the 16 case study lakes. Low concentration ranges are presented inset for each case to provide an assessment of baseline changes in TLa and FLa concentrations following a Phoslock® application. Peak values reported during the Phoslock® application are also reported, where available.

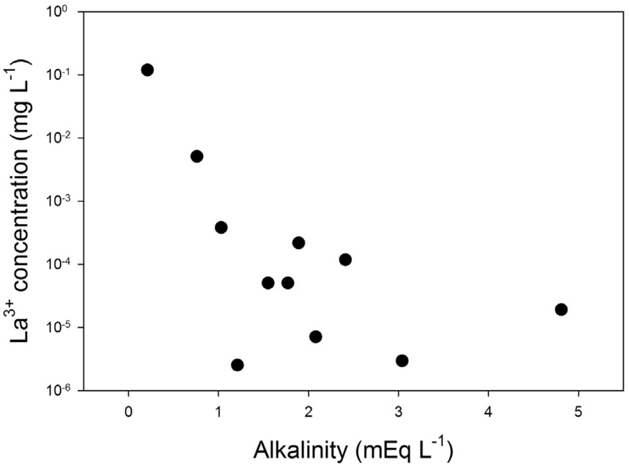

Fig. 4 – Variation in La^{3+} concentration with annual mean alkalinity in 11 lakes that have been treated with Phoslock®. La^{3+} concentrations were predicted using chemical equilibrium modelling (CHEAQS PRO). Input variables were mean annual pH, total lanthanum concentration immediately after application inferred from product dose estimates, Ca^{2+} and $CO_3{}^{2-}$ concentrations derived from mean annual alkalinity and phosphate concentrations.

4. Discussion

4.1. *Characterising the lanthanum recovery trajectory*

Results of GAM analyses indicated that recovery trajectories for TLa and FLa in surface and bottom waters in lakes following an application of Phoslock® were well represented by a 2nd order decay relationship, with time, and that recovery reached an end-point between 3 and 12 months post-application. However, inspection of the raw data (Fig. 3) also indicates the occurrence of sporadic increases in TLa concentrations in later months (e.g. month 18; Fig. 3a and c), and that these increases were not matched by increases in FLa concentrations. PCA analysis indicated that the maximum and minimum reported bottom water TLa concentrations varied negatively with water depth. These sporadic events may be the result of bed disturbance in shallow lakes and may not be related to diffusive release of FLa from sediments, as indicated by the low FLa concentrations. However, FLa concentrations in earlier months cannot be related to bed disturbance. Possible reasons for the increase in FLa concentrations following application include (1) ion-exchange/interaction between La in the carrier and an ionic composite of lake water; (2) dissolution of residual La in the product, not bound within the clay matrix, following wetting; and (3) error associated with FLa sample preparation where flocs of particulate La may pass through filters used to operationally

Table 3 – Summary of generalised additive modelling (GAM) results for surface and bottom water total lanthanum (TLa) and filterable La (FLa) recovery trajectories across the 16 lakes.

Response variable	r^2_{adj}	N = …	P value	Deviance (%)	Recovery time (months)	End point value (mg L^{-1})
Surface water TLa concentration	0.50	237	<0.001	64.5	8	0.007
Surface water FLa concentration	0.31	77	<0.001	67.8	3	0.004
Bottom water TLa concentration	0.32	178	<0.001	42.4	11	0.024
Bottom water FLa concentration	0.27	31	<0.001	63.9	12	0.001

separate dissolved from particulate La fractions in lake water samples.

The strong and negative co-variation reported between annual mean alkalinity (and also conductivity and pH) following application and the maximum reported TLa concentrations in surface waters indicates variation in settling rates associated with the lake specific physicochemical conditions. For example, Ketchum and Weber (1974) discuss in detail the complex relationships between alkalinity, calcium ion concentration, dissolved P concentration and the settling rate of bentonite in an experimental system, and report that interaction between Ca^{2+} and PO_4^{3-} ions can regulate the clearance of bentonite from solution at pH > 8. This interaction was attributed to the formation of hydroxylapatite which aids coagulation (Ketchum and Weber, 1974) and similar interactions may be expected within the Phoslock® matrix (i.e. with Si or Al complexes) explaining the apparent enhancement of settling at high alkalinity.

The complexity of such ionic interactions with regards to the performance of Phoslock® is also demonstrated by Haghseresht et al. (2009) who attribute a decrease in P binding capacity of Phoslock® by 29% at pH 9, when compared to pH 5 to 7, to changes in the dissociation of dissolved P (from dominance of $H_2PO_4^-$ to HPO_4^{2-}) and a greater affinity of solid phase La for $H_2PO_4^-$. Although the results presented in both the current study and by Haghseresht et al. (2009) cannot be used to infer cause–effect relationships, taken collectively they indicate the complex role of ionic interactions between carrier

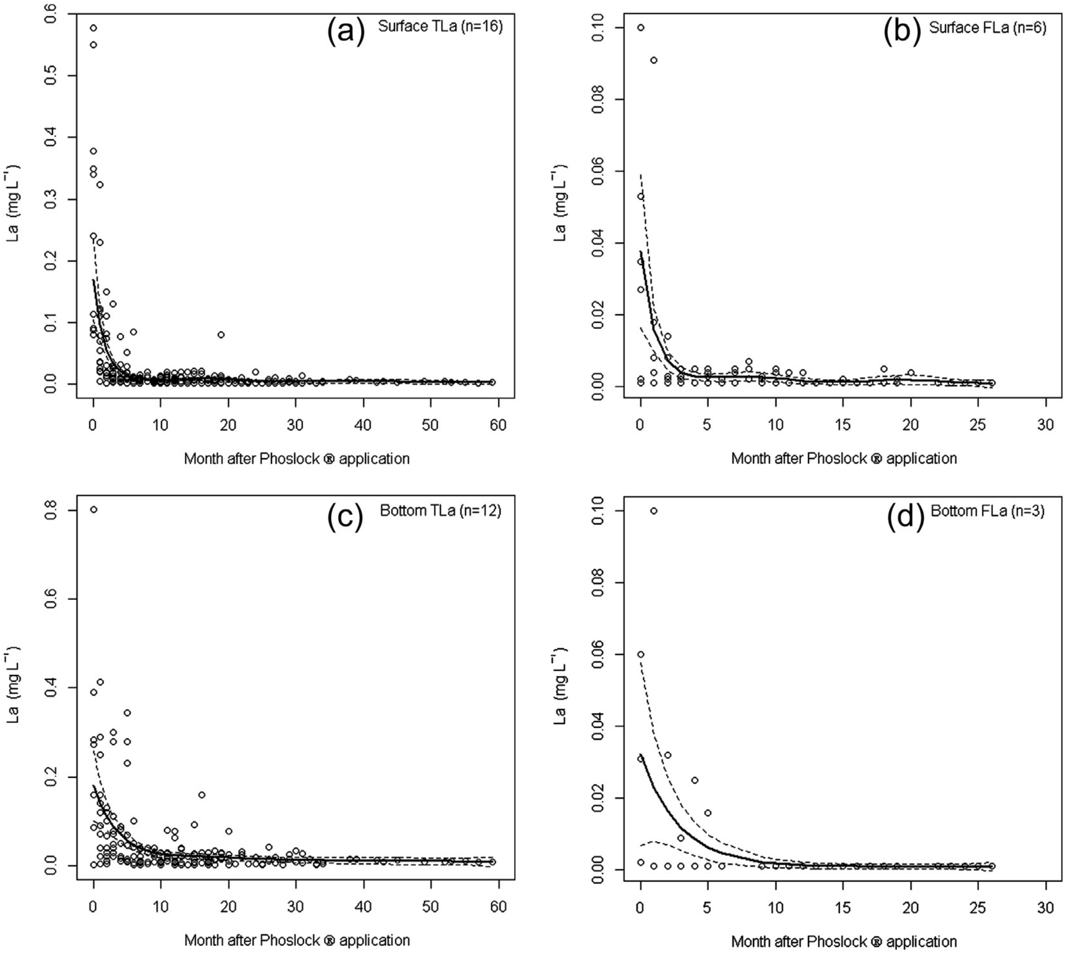

Fig. 5 – General additive modelling plots for total lanthanum (TLa; panels a & c) and filterable La (FLa; panels b & d) concentrations in surface (panels a & b) and bottom waters (panels c & d) following an application of Phoslock® across the 16 case study lakes.

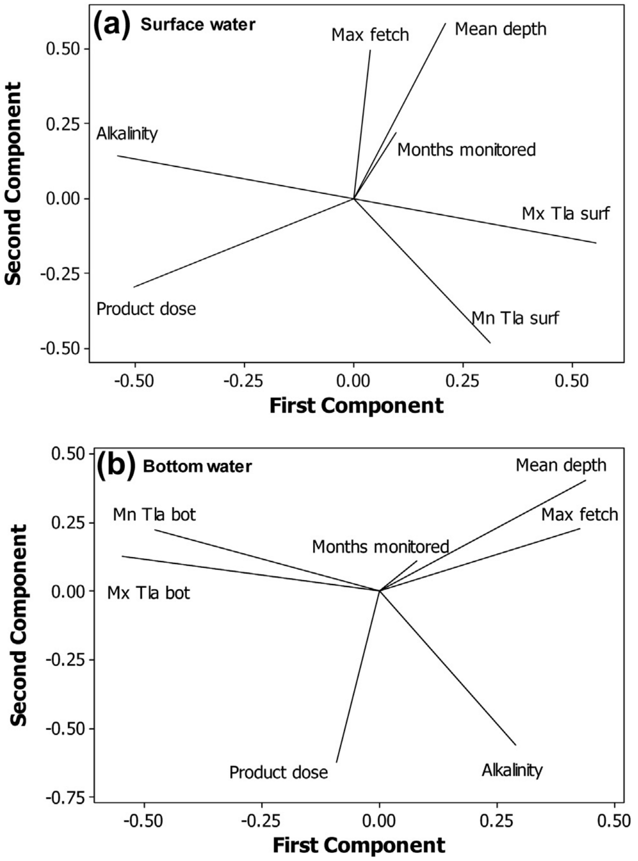

Fig. 6 – Results of principal components analysis for surface (a) and bottom waters (b) showing the weightings and ordination of each environmental variable measured along both principal components. Alkalinity – annual mean alkalinity following application; Months monitored – length of post application monitoring period in months; Mx – maximum value, Mn – minimum value; TLa – total lanthanum concentration; surf – surface water; bot – bottom water; Product dose – mass of product applied per volume of lake water; Max fetch – maximum fetch of the lake. PC – principal component; EV – eigenvalue; CV – cumulative variance explained. Surface water: PC1 – EV, 2.57; CV, 0.37, PC2 – EV, 2.19, CV, 0.68. Bottom water: PC1 – EV, 2.81, CV, 0.40; PC2 – EV, 2.21, CV, 0.72.

(i.e. Phoslock®) and ionic solution (i.e. lake water) in regulating settling rate and P uptake. From a practical perspective, these results indicate that factors other than the initial volumetric dose of Phoslock® appear to be more important in regulating the settling rate and P mass-normalised uptake capacity of La. Physicochemical conditions of receiving waters should, therefore, be considered fully in the context of product performance, prior to product application.

What is clear is that different processes are likely to dominate water column TLa and FLa concentrations during different phases of recovery following an application of Phoslock®. In the few months following an application, the decrease in TLa concentration in the receiving waters appears to be driven by product settling and site specific physicochemical factors. Following the rapid decrease in TLa concentration, sporadic events of increased TLa in later months, especially in bottom waters, are most likely driven by physically and biologically induced bed sediment disturbance processes in shallow lakes (e.g. Hilton et al., 1986; Lesven et al., 2009; Chaffin and Kane, 2010; Roskosch et al., 2011). It is likely that the rapid reduction in FLa concentrations in the early months is regulated through ionic interactions with constituents of the receiving water (e.g. $H_2PO_4^-$ to HPO_4^{2-}) and that the rate of loss may be regulated by physicochemical conditions of the receiving waters (Diatloff et al., 1993).

4.2. *The potential for ecotoxicological impacts*

Although rapid recovery was apparent in FLa concentrations in both surface and bottom waters, FLa concentrations did not fall below detection (i.e. pre-application concentrations of <0.001 mg L^{-1}) in the surface waters of at least two of the sites considered in this study, for the duration of monitoring. When compared to the range of EC50 values summarised in Table 1, the reported surface water FLa concentrations exceeded the threshold of 0.08 mg L^{-1} reported for *Ceriodaphnia dubia* (Stauber, 2000) in Loch Flemington (during the application) and in Niedersachsen Lake during the two months following the application. These concentrations decreased to 0.002 and 0.001 by post-application month 6 in both lakes. Of the countries included in this study, only The Netherlands has a legal maximum permissible concentration of FLa (0.01 mg L^{-1}; Sneller et al., 2000) and TLa in surface waters (0.15 mg L^{-1}; http://apps.helpdeskwater.nl/normen_zoeksysteem/normen.php; 7th June 2013). The Dutch FLa standard is based on studies specific to the assessment of reproductive rates in *Daphnia magna* (NOTOX 139499; available through the authors), the validity of which has been questioned in the literature (Lürling and Tolman, 2010; Lürling, 2012). Nevertheless, two of the three monitored lakes would have failed this FLa standard for bottom waters within the first month of post-application monitoring, FLa concentrations in both lakes fell below the Dutch standard between 1 and 6 months following application. In surface waters, five of the six monitored lakes would have failed the Dutch standard during the application however FLa concentrations in all lakes were below the standard 3 months following the application.

The range of Phoslock® concentrations in receiving waters can also be estimated as suspended solids (i.e. 0.62–46.0 mg L^{-1}). When considering both methods of estimating Phoslock® concentration in receiving waters it is clear that maximum values did not exceed the EC50 values reported for Phoslock® from the laboratory based ecotoxicology trials (lowest EC50 of 871 mg L^{-1} for *Daphnia* Lürling and Tolman, 2010; NOEC of 100 mg L^{-1} and EC50 of 150 mg L^{-1} for *Brachionus*; Van Oosterhout and Lürling, 2012) in any of the treated lakes. However, when considered as suspended solid concentration inferred from Phoslock® load or TLa concentrations, the values and durations of exposure reported here for Phoslock® have been shown in other studies to negatively impact the functioning of a range of components of the aquatic food web (Bilotta and Brazier, 2008). In addition, water quality guidelines for short term exposure (typically 24 h) of surface waters to increased suspended solids concentrations above background levels for the USA (National Recommended Water Quality Criteria US EPA, 2007), Canada (Canadian Environmental Quality Guidelines for Protection of Freshwater Aquatic Life (CGME), 2007) and the European Union (Freshwater Fisheries Directive, 2004/44/EC and 2004/44/EC) range from 5 mg L^{-1}–25 mg L^{-1} (Bilotta and Brazier, 2008).

In general, both the FLa concentrations that were measured following Phoslock® treatments and the free La^{3+} concentrations predicted by the CHEAQS PRO model were higher in soft waters when compared to hard waters, which may explain the differences in toxicity found in studies with freshwater zooplankton (Table 1). Since only part of the La-ions will be dissociated from the clay matrix after application and many more oxyanions such as phosphate and other ligands (like humic acids) will be available in natural waters, both the measured FLa concentrations and the predicted La^{3+} concentrations most probably represent overestimations of the actual free La^{3+} concentrations in the treated lakes. Of the 11 lakes included in the CHEAQS PRO model, 10 had alkalinities of 0.8 mEq L^{-1} or higher with each of these lakes having a maximum predicted concentration of free La^{3+} ions of less than 0.01 mg L^{-1}, substantially lower than the lowest reported EC50 concentrations for daphnia species. This indicates that the abundance of free La^{3+} can be expected to be very low in moderately low, normal and high alkalinity waters. Indeed, this is confirmed in several ecotoxicological studies which indicated no adverse effects of Phoslock® application under these conditions (e.g. Clearwater, 2004; Watsun-Leung, 2008; Lürling and Tolman, 2010). Applications of Phoslock® in very soft water, on the other hand, should be met with more care, particularly in the absence of phosphate ions.

In lakes characterised by both low alkalinity and low phosphate, the common assumption that La will not be 'bioavailable' after an application of Phoslock® should be more comprehensively assessed over longer study periods and the mechanisms of incorporation into the tissues of organisms identified. Results from previous incorporation bioassay research should be used to underpin this work (e.g. *Cyprinus carpio*, Tu et al., 1994; *Oncorhynchus mykiss*, Landman and Ling, 2006). The role of behaviour in aquatic organisms should also be incorporated into risk assessments when considering the use of Phoslock® in low alkalinity lakes, where benthic dwelling organisms may be expected to be exposed to higher La concentrations than pelagic organisms.

We have highlighted issues with comparability of potential ecotoxicological impacts between sites and between potential metrics (i.e. TLa, Phoslock® and FLa concentrations). The issues discussed here for Phoslock® of poor comparability between ecotoxicological tests are not uncommon (Jančula and Marsalek et al., 2011; Bilotta and Brazier, 2008). One of the major issues in the available ecotoxicological data is the lack of consistent use of test solution, especially as the results of the present study, and others (Lürling and Tolman, 2010), indicate that the physicochemical composition of the receiving waters can significantly alter ecotoxicological sensitivity to Phoslock®. To reduce uncertainty when considering the potential ecotoxicological impacts of a Phoslock® application at sites for which the risks can be identified (e.g. very low alkalinity, low phosphate), it is recommended that a phased experimental approach be employed which begins with laboratory based trials on indicator organisms, and where an acceptable impact is reported, is followed by *in situ* mesocosm trials to assess impacts on populations and ecosystem functioning prior to full ecosystem application (Mayer-Pinto et al., 2010). Alternatively, the lake may be allowed to recover naturally following catchment management.

4.3. *Implications for monitoring and eutrophication management programmes in lakes*

This study indicates that there is a general lack of high frequency long-term TLa and FLa monitoring data in case study lakes and that, where available (i.e. of the 16 case study lakes identified), the monitoring frequency, sampling and analytical methodology, and determinands included in the monitoring programme are inconsistent. Our results indicate that the recovery characteristics of FLa and TLa are dependent on a range of lake specific traits and are determinand specific, however, our analysis is by no means fully comprehensive as a result of a general lack of site specific data (e.g. hydraulic retention time and weather data). A site specific approach is required when planning future monitoring programmes to assess the responses of TLa and FLa following Phoslock® applications. When designing a post-application monitoring programme to assess recovery, it is essential that the monitoring period extend beyond the likely transient recovery period. Of the 16 lakes included in this study 3 lakes reported a maximum monitoring period of less than the recovery periods estimated in this study. This is a common artefact of post-treatment monitoring in many lake restoration studies reported in the peer reviewed literature (Verdonschot et al., 2013).

It is important that the information on potential impacts of Phoslock® be available to policy makers and water quality managers to underpin decisions on the use of such products (Gibbs et al., 2011). This information should be based on comprehensive and objective documentation of chemical and ecological responses and should be conducted across a range of experimental scales, from laboratory mesocosm to whole ecosystem (Schindler, 1998). Of particular importance is the consideration of case studies in which the responses were unexpected, or there was no obvious response (e.g. Meis et al., 2012; Van Oosterhout and Lürling, 2011). The results of the current study highlight some important practical implications for water managers including (1) limit the daily dose of Phoslock® to below the thresholds for suspended matter effects on ecosystem components outlined by Bilota and Brazier (2008); (2) shallow lakes of very low alkalinity may be more sensitive to sustained conditions of high TLa concentrations (i.e. low settling rate) when compared to deeper high alkalinity lakes and so the seasonal behaviour of key components of the food web should be considered when planning an application, (3) when estimating dose, the potential implications of the physicochemical conditions of the receiving waters on performance of the product should be fully considered and site specific lab based trials are recommended to confirm dose estimates based on system P mass balances; and (4) in order to quantify the potential for ecological impacts in treated lakes, it is essential that TLa and FLa concentrations be monitored at least monthly, and in surface and bottom waters, for more than 12 months.

5. Conclusions

- It was confirmed that release of FLa to the water column following Phoslock® application does occur, with peak FLa concentrations during application reported up to 0.414 mg L^{-1}.
- Results of the GAM analyses indicated that recovery was achieved within 3 months in surface waters and 12 months in bottom waters, although the FLa GAM models were based on a relatively low number of case study lakes.
- Maximum reported estimates of Phoslock® in receiving waters did not exceed the EC50 values for Phoslock® reported by others and based on laboratory trials.
- Estimated La^{3+} concentrations were predicted to be relatively low in moderately low to high alkalinity waters and no direct toxic effects were likely in the treated lakes. In lakes with very low alkalinity and low concentrations of phosphate and other oxyanions, this might be different and a more mechanistic understanding of the incorporation of La into the tissues of aquatic organisms is required.
- The mechanisms of P incorporation onto La embedded within the bentonite matrix should be published, as should the physicochemical drivers of these mechanisms.
- It is essential that water managers consider the impacts of the physicochemical conditions of receiving waters, both in terms of product performance (i.e. P uptake kinetics) and cost effective dose procedures.

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Marine Biochemists
2940 E. La Jolla St. #B, Anaheim, CA 92806
714/632-5253   Fax: 714/632-3419   www.marinebiochemists.com

June 20, 2019

Dennis,

Here is synopsis of the conversation I had with W. Russell Norman, P.E., Water Resources Control Engineer, North Basin Regulatory Unit.

W. Russell Norman stated that he can start processing your permit as soon as he receives Form 1, Form 2E and the technical report. He understood your need for the use of Alum or Phoslock to control nutrients. He stated that the technical report for Alum would be a lot more complicated than that for the Phoslock do to the fact that they would require sedimentation sampling for the effect or potential effect on all the organisms found. This would require a species analysis test for the sediment and the water column prior to any application. Based on the finding separate tests would need to be conducted on the effect of Alum to growth, reproduction and any other aspect deemed necessary. Since Phoslock does not contain any heavy metals, the technical report on how to monitor the ecosystem for potential effects would be not be as extensive and expensive. Mr. Norman stated he would try to find a sample of a technical report for you to review. He is also willing to work with your staff in producing the technical report to the specification they require.

Sincerely,

Curtis Cress
Branch Manager/Aquatic Biologist
Marine Biochemists/Innovative Water Care LLC.

From:	Terry McNabb <tmcnabb@aquatechnex.com>
Sent:	Tuesday, January 22, 2019 5:05 PM
To:	Dennis Teece
Subject:	first draft APAP
Attachments:	APAP for Spring Valley.docx

Attached is the first draft of this APAP. you ought to give it a look and offer comments. When we put into PDF will add pictures and other graphics.

Two things that are important.

1. The alum and phoslock options that you are interested in are not on this permit and as such it can't provide coverage to apply them. This permit is for the use of US EPA registered aquatic pesticides. Alum and Phoslock are not pesticides. In addition, this permit lists the active ingredients that are covered and these two compounds are not on there. What I have done is placed these compounds into the alternative to pesticide section where we call them phosphorus pollution mitigation strategies. This tells them you are using them and that might be enough. So basically you can't get coverage under this permit to use either of these. hopefully they won't require a separate permit because they would have to develop it.

2. The Lahonaton Board has an additional issues that isn't present in any of the other state board regions, they required an exemption from their regional regulations, and they haven't told us yet how they will do that. they were supposed to have a meeting I think at your place sometime before the first of the year. We need to nail that down as well as get this filed with them.

Lastly, until the new guy got there, the person reading these plans was making a number of comments that indicated an anti herbicide bias. The requirement under the permit is to develop a plan that meets the guidelines and file and follow it, they aren't supposed to nit pick them when they come in. I am going to take a second cut at this and will also incorporate any comments you have into it.

Terry McNabb
Manager/Aquatic Biologist
www.aquatechnex.com

AQUATIC PESTICIDE APPLICATION PLAN

Prepared in support for Coverage Under

California Statewide General Nation Pollutant Discharge Elimination System (NPDES) Permit for Residual Aquatic Pesticide Discharges to Waters of the United States From Algae and Aquatic Weed Control Applications. Water Quality Order No. 2013-0002-DWQ General Permit No. CAG990005 (As amended by Orders 2014-0078-DWQ and 2016-0073-EXEC)

Submitted to:

State Water Quality Control Board

December 2018

Prepared on Behalf of:

Spring Valley Lake Association

Victorville, CA

Prepared by:

Aquatechnex, LLC, 2025 South Lyon Street, Santa Ana, CA 92705

www.aquatechnex.com

760-636-8267

Introduction and Background Information

This Aquatic Pesticide Application Plan (APAP) has been prepared in compliance with the Statewide General National Pollutant Discharge Elimination System (NPDES) Permit for the Residual Aquatic Pesticide Discharges to Waters of the United States. The submission of a APAP is a requirement of this permit. This document is a comprehensive plan that identifies the setting, approach, monitoring and reporting required for the use of aquatic pesticides in Spring Valley Lake, California.

The use of aquatic pesticides are considered to be tools and part of a larger set of lake management practices and planning. The lake owner, Spring Valley Lake Association, is charged with protecting the beneficial uses of this water body that include water sports, waterskiing, recreation, swimming and fishing.

Lake Setting

Spring Valley Lake is the centerpiece of a Boise Cascade Home and Land Corporation development in Victorville, California. The land was purchased from the Kalin Ranches, who used the property primarily for cattle ranching and irrigated framing. Boise Cascade broke ground for the community development in March of 1969 giving life to the 2,007 acre development and community.

The community included an 18 hole championship golf course, an Equestrian Center and the lake. There are approximately 4,313 lots within the community. The developer turned over management of the community to the Spring Valley Lake Association in 1973. The community is managed by an elected board of directors. The day to day operations of the community are performed under the direction of the general manager and the departments that serve the community. In addition, there are committees made up of appointed residents that assist management in the operation of the community.

Construction of the lake began in June of 1069. The excavation of the lake basin was one of the larges earth moving projects in the history of the Victor Valley at that time. Boise Cascade began filling the lake in January of 1970, taking approximately one month to complete

A historic video of the lake construction process can be viewed at this YouTube site.
https://www.youtube.com/watch?time_continue=9&v=lJh3acOHzhQ

Spring Valley Lake is an artificial lake with a surface area of 200 surface acres, has about 7 miles of shoreline and ranges from depths of 9 to 22 feet. It is located just outside of the community of Victorville, CA in San Bernardino County.

The lake is located adjacent to the Mojave River. The primary water sources entering the lake are community wells permitted to provide fill water to the lake, surface runoff from the surrounding 9 sq. miles of develop land during rain events which is annually 6” of precipitation and in recent years excess water discharged from the local State Fish Hatchery. The lake can discharge to Mojave Narrows County Park lakes through a controlled outlet. As Mojave Narrows Park Lakes are considered part of and adjacent to the Mojave River, even though the lake is an artificial water body the discharge from the lake when it occurs can be considered a hydraulic connection to Waters of the United State. Hence a NPDES permit can be required for some of the management activities that might be required to mitigate aquatic pest problems in the lake.

The lake provides a number of recreational opportunities to the community. The primary function of the lake is waterskiing. It is considered one of the premier waterskiing communities in the Western United States and one of the primary reason's residents choose to live here. The lake has a marina and fuel facility. There is a swimming beach that provides opportunities for recreation and swimming lessons. There are three parks in the community. There are also 14 fishing locations around the margins of the lake and the Association manages the fishery to insure sustainability.

During the 1980's the lake became infested with the invasive aquatic weed Eurasian Milfoil. As the lake is primarily all littoral area, the majority of the 200 surface acres were infested. This growth had a dramatic effect on the beneficial uses of the lake and posted a safety threat to swimmers and water-skiing activities.

Spring Valley Lake Association invested in several aquatic vegetation harvesters and for a number of years operated an aquatic plant removal program. This activity was found to be expensive and production rates of the harvesting equipment could not keep up with the growth of the invasive weed.

Sometime in the late 1990's, the Association contracted with an aquatic herbicide applicator and those treatments largely removed aquatic vegetation from the lake. The lake experiences a shift to a planktonic alga dominated system in this time frame.

In 2010, the community developed a Water Clarity Improvement Program that has a goal of restoring clarity to the lake system and to bring back populations of native aquatic plant species. Water clarity was limiting the ability of the lake to support aquatic plant populations. This plan involved ongoing monitoring, management of cyanobacteria blooms through phosphorus mitigation programs and planting aquatic vegetation.

This program has been ongoing for several years since. In the past few years, there have been problematic blooms of potentially toxin producing cyanobacteria in the region.

Regional Water Board staff collected surface water samples at Spring Valley Lake on June 13, 2018. Lab results indicate low levels of cyanotoxin (anatoxin-a). Based on the laboratory results and site indicators (visible algae, blue-green color) that were observed by the sampling crew, Water Board staff recommends the Spring Valley Lake Homeowners Association advise people, who may be recreating in the impacted water, of the potential health risk. The Caution Signs also advises pet owners to not let pets go into or drink the water or eat scum on the shore.

This condition has triggered the development of this Aquatic Pesticide Application Plan and a program to manage cyanobacteria blooms into the future.

Nuisance Conditions Present

The primary nuisance condition present in the past few years at Spring Valley Lake have been harmful algae blooms (HAB). These blooms post a threat to the health of those recreating on and near the lake. They pose an acute threat to pets and wildlife that might advertently drink from the lake during toxin producing events. These conditions can also have an economic impact on the community depressing property values, causing cancellation of family or community events and creating regional press stories that perspective residents might see.

In recent years, the State Water Quality Control Board has become increasingly concerned about HAB's in lakes state wide. They have started a program of sampling and reporting toxic events through their HAB Incident Reports Map online at https://mywaterquality.ca.gov/habs/where/freshwater_events.html . This has included several visits to Spring Valley Lake and in June of 2018, the posting of a caution advisory on this web site for low levels of *anatoxin-a* and the recommendation that the community advise people that may be recreating in the impacted water of the potential health threats. They also recommended and published on this web site the need to post caution signs advising pet owners to not let pest go into or drink the water or eat scum on the shoreline.

This elevated the level of concern in the community and the Association in order to mitigate this danger may need to treat with US EPA registered algaecides to manage the threat. This work would be done within the framework of an integrated program that addresses root causes and considers all appropriate technologies to mitigate toxic algae blooms

The focus of this program will be to address cyanobacteria blooms and help mitigate the treat posed by these toxin producing organisms

Aquatic Plant Nuisance Conditions

Normally when an APAP is developed, the primary objective is to manage submerged or marginal aquatic weed growth. Spring Valley Lake Association has been for several years attempting to encourage the re-establishment of submerged aquatic plants in the lake. Several factors have contributed to the loss of vegetation in the lake. Primarily water clarity and limited light penetration have been the cause of this loss over time. The Community has an active plan to restore aquatic plant growth in the lake that includes mitigation of problem algae blooms and suspended materials. At this point there is no interest in treating and controlling submerged aquatic weed growth with aquatic herbicides.

In recent years however, there has been a growing problem with cyanobacteria. These organisms thrive in lakes that are classified as eutrophic or hyper eutrophic. Cyanobacteria blooms are a growing problem in California Waters. Cyanobacteria, or blue green algae, have been in the environment for billions of years and are a natural part of freshwater aquatic ecosystems. In waters with lower trophic states, they can be an important part of the ecosystem performing a number of functions including being a food source.

As lakes receive and accumulate nutrients they shift from aquatic plant dominated communities to planktonic algae dominated systems. Phosphorus levels in particular have an impact on the competitive ability of cyanobacteria species to compete for space with other forms of algae. As cyanobacteria can convert nitrogen from the atmosphere, increasing levels of phosphorus can give them a significant competitive advantage. This appears to be happening in Spring Valley Lake.

When conditions are favorable for cyanobacteria, these single celled organism expand rapidly and cause "bloom" conditions.

Cyanobacteria can and do produce a number of compounds that have both acute and chronic toxicity potential if ingested. These toxins pose a direct threat to human health. They can impact the safety of people using lakes and river systems for recreation. They can impact delivery of potable water from reservoirs where blooms are occurring. Pets and wildlife are most susceptible to this threat. The acute toxins can be both liver and neural toxins. There are numerous cases of acute poisoning of pets and wildlife annually. California reports that in 2017 there were 25 domestic animal deaths, numerous fish and wildlife fatalities and 8 incidents of human reported illness.

The chronic affects of these toxins is also now recognized. Compounds produced by these species are directly linked to Lou Gehrig's Disease or ALS. There is also documented evidence that these compounds can aerosolize and expose humans near affected lakes over time. Spring Valley Lake is subject to wind events often daily.

The objective of this APAP is to provide the guidance and legal authority to manage these toxic algae blooms and maintain safety of human health to those living adjacent to and recreating on the lake.

Examination of Alternative Approaches for Nuisance Condition Management

While there are a number of control options available for the management of vascular aquatic plants, tools to manage cyanobacterial blooms are limited at the time of this plan development.

Biological Algae Control Options for Lakes

There are no effective biological control tools available to manage planktonic algae blooms currently.

Mechanical Algae Control Options for Lakes

There are no effective mechanical control technologies available to manage cyanobacteria blooms currently. Spring Valley Lake Association has however a considerable amount of capital and operational investment in a lake aeration system. These technologies can help mitigate sediment release of phosphorus through destratification and the maintenance of good dissolved oxygen levels from top to bottom in the lake water column. Legacy phosphorus can accumulate over the decades the lake is form in the lake sediments. In the absence of dissolved oxygen at the sediment water interface phosphorus can be mobile at certain periods of the year. Maintaining dissolved oxygen via the aeration system helps mitigate phosphorus release from the lake sediments that will contribute to conditions that favor cyanobacteria. This investment in a mechanical solution has contributed to and will continue to contribute to phosphorus mitigation. It has not however in recent years been able to prevent bloom conditions.

Physical Algae Control Options for Lakes

There are no physical control technologies available to manage planktonic algae blooms. These single celled organisms can not be collected or physically removed from the lake water column using existing technology.

Cultural Algae Control Methods for Lakes

While there are no cultural practices that can remove cyanobacteria from a lake system, Spring Valley Lake Association has invested in cultural removal of invasive carp from the lake. European Carp were introduced and have established a reproducing population over time. This fish species is a bottom feeder, carp will capture a mouth full of lake sediment, sort out the benthic organisms that are food sources and expel the sediment to the water column. One fish doing this will mobilize sediment phosphorus at a level that would probably not be noticed, but as the population explodes this contribution can be significant. Spring Valley Lake Association identified this in its lake management program and began to contract for removal of carp from the lake via commercial fishers. In recent years the community purchased a fish shocking vessel and regular performs carp removal. While this removal has been significant and has benefited the lake generally, it has not to date reduced phosphorus levels that have eliminated cyanobacteria bloom conditions.

Nutrient Management Method for Lakes

There are two in lake phosphorus pollution mitigation technologies that the Association is interested in implementing in conjunction with limited US EPA Registered Algaecide treatments as necessary. Preventing these blooms is a key strategy and is widely used in California as a Best Management Practice. As phosphorus is the limiting nutrient in most cases for cyanobacteria, sequestering phosphorus in lake reduces the carrying capacity of the system to support these single celled organisms that must get their nutrition from the water column. It also reduces the competitive advantage that cyanobacteria have over more beneficial species of planktonic algae.

These products are not considered pesticides or subject to regulation under the case law that requires an NPDES permit for the application of US EPA Registered Aquatic Pesticides that leave a chemical residue after they complete their intended tasks when applied to waters of the United States. They are phosphorus pollution control technologies that have been developed under the direction and funding of the US EPA's Clean Lakes Program. In Southern California, these technologies are most widely utilized within the Santa Ana Regional Water Quality Control Board's Jurisdiction. That Board has determined that permits are not necessary to target and sequester phosphorus pollution to lakes within that region.

The first of these is Aluminum Sulfate. This material is applied to the lake surface, it forms a precipitate or floc that settle rapidly through the water column and captures free reactive phosphorus through a tight bonding process. Phosphorus is thus stripped from the water column and sequestered within floc. The floc settles onto the lake bottom and effectively caps or traps phosphorus that might be mobile from those sediments as well. Aluminum Sulfate is commonly used in the treatment of potable water.

The second of these technologies is Phoslock. This technology was developed by the Australian National Science Academy to help mitigate phosphorus pollution driving cyanobacteria blooms in that nation in the 1990's and since commercialized. Lanthanum is the sequestering technology in this application. This rare earth element has a very high affinity and binding capability for free reactive phosphorus (FRP) in surface waters. Phoslock is also applied to the lake surface and the material settles through the water column capturing the FRP and rendering it biologically unavailable basically forever.

These two technologies are preventative in nature. The levels of phosphorus present in the water column drive cyanobacteria growth, bloom conditions and carrying capacity of the lake to shift to these problematic species. Using these preventative technologies significantly reduce the need to apply chemical control technologies such as US EPA Registered Algaecides.

Chemical Control Technologies for Algae Control in lakes

One of the more effective management techniques for treating cyanobacteria blooms is the use of US EPA Approved Algaecides. Algaecides are generally applied when conditions warrant targeting and removing blooms present. These treatments remove cyanobacteria biomass from the water column. They are not preventative in nature, they are used to react to cell counts that exceed target thresholds. These threshold are set for species present and cell density present. When these levels are exceeded an algaecide it use to remove the growth and bring call counts back under treatment thresholds.

Copper algaecides are the most widely used products in the market. Copper when ingested by algae cells disrupts key cellular processes and the cells parish.

Copper in the form of copper sulfate is the first and sometimes current technology applied to treat problem algae growth. Copper sulfate is fairly unstable in harder waters present in most of California. When applied, the copper sulfate reacts with the calcium carbonate present in the lake water, forming a new compound copper carbonate. Copper carbonate is insoluble and sinks rapidly out of the water column. This can dramatically reduce the contact and exposure time necessary to effectively get into the target cells that will be in the upper portion of the water column where light is the best.

Chelated copper algaecides are the preferred products to use when a copper algaecide is selected. These materials are designed to remaining available to the target algae cells and increase contact exposure time. This results in higher kill rates and over the summer will reduce the need to use an algaecide. Many of these products also have penetrating agents and infusing technology that will help the copper move into the cells effectively even when targeting some of the more resistant strains. Captain XTR algaecide is a good example of a product that would be used in this role.

Chelated copper algaecides can be used in potable water reservoirs and have no water use restrictions for treated areas.

Hydrothal 191 is a endothall based algaecide that is very effective against cyanobacteria. It is a liquid based algaecide that is applied at low rates to the lake surface or top 3-4 feet of the water column. Hydrothol 191 is also a labeled and used as a herbicide at higher application rates. This product can be used with minimal restrictions on the use of treated water. At algacidal application rates there is margin of safety for fish, at herbicidal rates this product can cause impacts to fish. When treating with Hydrothol it is important to start at the shoreline or the end of fingers and work out so fish are not trapped and can avoid contact with the material in the water.

Peroxygen algaecides are also every effective against cyanobacteria. Some of the more beneficial green algae species are more tolerant of this chemistry so it can select for the HAB's present in the system. The final case law that required the need for an NPDES permit to apply aquatic pesticide stated that "while the application of an aquatic pesticide that is registered for use in aquatic environments by the US EPA should not be considered the discharge of a pollutant with respect to the Clean Water Act, any chemical residue left after the product has completed its intended purpose could be considered a pollutant and subject to regulation under the Clean Water Act". Peroxygen algaecides oxidize the cells and the byproducts are oxygen and water so there is no chemical residue left in the water column after the product has completed its intended purpose of killing the algae cells.

Peroxygen algaecides such as PAK 27 can also oxide the organic toxins that are created by cyanobacteria. There are published scientific journal articles that document significant reduction in both cell counts and toxin levels following peroxygen algaecide applications.

Algaecide applications should be performed under the direction of a licensed applicator with an aquatic endorsement issued by the California Department of Pesticide Regulation. The applicator should follow the direction and requirements of the NPDES permit that govern applications of waters of the State.

Discussion of Factors Considered when Selecting Management Options

The primary factor to consider is that cyanobacteria post a threat to the health of nearby residents, water user, pets and wildlife. The system should be managed to remove or mitigate this threat as much as possible. Of the options that will provide relief, each should be applied as appropriate as part of an integrated algae management program.

The decision to use the mechanical technologies ie aeration has already been made. The community has invested in the purchase and installation of a system that serve the entire lake. This system operates continually and provides improved water quality with a focus on mitigating sediment legacy phosphorus release.

The cultural technology program to remove European Carp has been implemented and is ongoing. The community originally contracted carp removal, they since have purchased a fish shocking vessel to perform this task. Shocking boats are generally used for fish survey work. The boats have a generator and electrodes that hang into the lake water that deliver a DC current to the water column. Those fish within the range of this discharge are temporarily stunned and float to the lake surface. When performing a fish are netted out of the lake, measured, tagged and revived and placed back into the lake. That data is used to calculate the health of the fishery. In the case of the invasive species European Carp, the fish are stunned, netted out and removed from the lake. The maintenance staff of the Association perform this work regularly throughout the year. There is a high focus on the period where carp spawn as they will congregate in the lake shallows and are easier to target and collect in greater numbers. This has had an impact on reducing the reintroduction of legacy phosphorus from the lake sediments.

While these practices can keep phosphorus out of the algae growth cycle, there are regular inputs from the watershed during the rainy season and from the effluent discharge from the State Fish Hatchery that is the primary water source for the lake.

This inflow should be addressed at least annually in the spring after rains conclude for the season. One of the in-lake phosphorus pollution mitigation technologies should be applied with the dose calculation based on sampling data that shows current levels. Sequestering phosphorus using Aluminum Sulfate or Phoslock will remove phosphorus from the water column and will reduce the need to perform algaecide applications dramatically.

In the event of blooms during the season that occur, one of the US EPA registered algaecides discussed could be applied.

Treatment areas at Spring Valley Lake, Discussion of Treatment Approach

Algae treatments should be selected and applied based on an assessment, prescription and implementation approach. This approach incorporates routine monitoring of the system for early detection of nuisance algae and dimensions of the infestation. These monitoring data are compared with a set action threshold levels, designed to preserve the objectives for the system. Upon exceedance, rapid implementation of an appropriate product and amount necessary to attain control is conducted. Monitoring continues for subsequent exceedances and need for additional treatments. Below is a general summary of our approach to treating cyanobacteria with a peroxide-based algaecide.

Assessment

With an effective monitoring program, a cyanobacterial infestation can be mitigated early in a bloom scenario. A well designed and implemented Algae Action Threshold Level (AATL) program is a proven solution that provides these water quality benefits; 1) lower biomass/ density of harmful algae, 2) less risk of high toxin levels being produced, 3) less risk of dissolved oxygen depletion following natural die-off a bloom or following treatment, 4) enhanced control/reduced speed of HAB recovery, and 5) less product and resources needed for control (short & long-term).

There are many options that can be implemented for monitoring the system depending on budget and time constraints. From visual observations, to in situ probes (e.g., Chlorophyll, Phycocyanin, turbidity) or actual grab samples shipped to the laboratory for confirmation of algal genera and densities.

Prescription: Action Threshold program

Action thresholds are designated levels that incite a treatment and are designed to preserve the objectives of the system. These can be adaptable based on dynamic environmental conditions. With the recreational, ecological and human health priorities of the system, we proposed some general guidance on these levels.

Results from the monitoring data would be compared with the action threshold levels to determine the need for a treatment. The threshold cyanobacterial density level we would propose for triggering a treatment would be 20,000 cells/mL of potentially toxic cyanobacteria. This is based on the WHO (1999) guideline densities for recreational levels and in line with proposed densities by the USEPA (2016). At this density level, even if cyanotoxins were produced or released with treatment, total levels would only decrease and predicted to be below guideline levels for human health (Note: guidelines are based on total toxin, not free). Treating the source of the toxins is much less risk than not treating as blooms will likely increase in total toxin, form aggregate ‘hot spots’ of toxin and eventually release anyway. Treatments of PAK 27 have shown rapid decreases in toxin levels following application (Sinha et al. 2018). There are many benefits as mentioned previously of setting conservative AT levels and initiating treatments early in a bloom.

A key aspect of this early detection and the rapid response is at these densities, the amount of PAK 27 that can control the targeted cyanobacteria is much lower and therefore more economical for product and more rapid application. A rate of around 20 pounds per acre-foot of water, this is equivalent to around 2ppm H_2O_2, can provide effective control of most planktonic cyanobacteria if treated at these lower densities. This rate would also have a large margin of safety for non-target zooplankton (Reichwaldt et al. 2012) and beneficial algae that may excel post-treatment (Drabkova et al 2007b). This could select for a beneficial algal assemblage that moves up the food chain and competes with the cyanobacteria to prevent re-growth to nuisance levels and need for subsequent treatment (Matthijs et al 2012; Weenink et al. 2015). This product can be applied in a manner to target portions of the water column as many cyanobacterial blooms are heterogeneously distributed. If this action threshold level is exceeded, a PAK 27 application will be put out within a week of the exceedance. The treatment zone will be based on quantitative results as well as visual analyses the day of treatment. Extra buffer acreage around the exceedance will be accounted for to ensure the bloom area is covered.

The top four feet of water is expected to be needed to target (potentially less depending on monitoring data). This would result in up to 80 pounds of PAK 27 per surface acre treated. Again, assuming treatment occurs at these lower densities. Higher algal densities/biomass would demand higher amounts of product. Large acreage treatments (>80) are expected to get longer term control due to potential for new algae to migrate back into the treated area.
Implementation

Treatment areas can range from localized accumulations in the channels or fingers of the lake, algae populations that are wind driven to a downwind shoreline or if necessary the entire lake. To minimize the need for sampling and to selectively target cyanobacteria an peroxygen algaecide should be the primary tool selected for these treatments when and where necessary.

> ***PAK® 27* algaecide** (USEPA registration number 68660-9-67690; *NSF/ANSI Standard 60 Certified for use in drinking water supplies; OMRI certified for Organic uses*) is the primary technology we are proposing to directly control harmful cyanobacterial blooms and associated toxins and taste/odor compounds. PAK 27 has been widely used throughout the US to control cyanobacteria in all types of aquatic sites (e.g., lakes, ponds, lagoons, bayous, canals, reservoirs, wastewater ponds; potable water sources,). PAK 27 is a peroxide-based algaecide that rapidly degrades post-treatment and leaves no residual (Bauza et al. 2014). An effective peroxide-based algaecide that can be used to selectively control cyanobacteria while having negligible impact to desirable algae and wildlife species. No water use restrictions are present during or after its application.

The applicator should be licensed and trained to make these applications.

Description of Lake Control Structures and their Operation

Water flow through this lake is governed by an agreement titled the Verde Ranch Group. The agreement governs delivery of water to the lake and through the lake to downstream water rights holder.

A primary source of inflow water to Spring Valley Lake is effluent water from the California Department of Fish and Game Mojave River Fish Hatchery. This facility is south of the lake and community.

The Hatchery has several wells and delivers the bulk of the effluent water through a stream system across the Spring Valley Lake Country Club and into the south end of the lake. The Hatchery can also discharge into the Mojave River Bed if necessary.

Spring Valley Lake Association also has a number of wells that can be used as necessary to maintain lake level and to insure downstream water delivery.

Water leaving Spring Valley Lake flows to the Mojave Narrows Regional Park and through a system of lakes the Park owns and onward to the Kemper Campbell Ranch.

A map of this system is attached here.

Monitoring Program

There are two types of monitoring that should be included in the efforts at Spring Valley Lake. The first is the data collection and analysis necessary to track conditions and trigger treatment response. The second type is that required and necessary to comply with the NPDES permit.

When aquatic pesticides are applied to the lake under the coverage and conditions of the statewide NPDES permit, sampling is required. The Association will implement a treatment sampling protocol based on the product selected for application and the requirements stated in the NPDES permit. The data sheet that captures the necessary information is attached as an appendix.

Record Keeping and Reporting

The Association will implement a record keeping and reporting program as required by the conditions set forth in the NPDES permit.

Additional Best Management Practices

The source of water for the lake will for the foreseeable future be nutrient rich and the integrated plan presented in this document will help mitigate the impacts that resulting cyanobacteria blooms would cause.

The community does have the option to restrict water flow from the lake to downstream water users with coordination. One additional best management practice will be to schedule treatments and close discharges from the lake during and for some period of time after each treatment. When using a Peroxygen algaecide this would not be necessary as there is no byproduct that would leave the lake. If a copper algaecide or endothall based algaecide are selected, the lake discharge should be managed until levels are below detection in the vicinity of the discharge point. This generally happens within 24-48 hours.