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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

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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 was evident in the post-application maximum TLa and FLa concentrations reported for surface waters between 0.026 mg L^{-1} to 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 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.

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., 2013). 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., 2013). 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 et al., 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 and 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 to 9, commonly reported in eutrophic lakes (Douglas et al., 2000; Haghseresht, 2006; Robb et al., 2003, Ross and Hagseresht, 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.

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?

METHODS

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.

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 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).

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 & 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*.

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

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*http://sepro.com/documents/Phoslock/TechInfo/Phoslock%20Technical%20Bulletin.pdf

PCA analyses were carried out using Minitab statistical software, version 14 (Minitab Ltd., Coventry, UK).

RESULTS

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 (Figure 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® (Figure 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} to 2.300 mg L^{-1} 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} (Figure 4). The concentration of La^{3+} decreased with increasing mean annual alkalinity of the receiving waters following an exponential decay function ($La^{3+} = 404.9629 \times \exp^{(-5.8179 \times \mathrm{Alkalinity})}$, $r^2_{adj} = 0.999$; $P < 0.001$).

Quantifying recovery trajectories for total and dissolved lanthanum following a Phoslock® application

Results of the GAM are shown in Table 3 and Figure 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.

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 (Figure 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.

DISCUSSION

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 (Figure 3) also indicates the occurrence of sporadic increases in TLa concentrations in later months (e.g. month 18; Figure 3c and d), 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 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 (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).

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 have 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 to 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 hours) 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} to 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, 2009; 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 Tollman, 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.

Implications for planning, 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 for 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 all 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 Billota 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.

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 reported for Phoslock® reported by others following a range of laboratory based ecotoxicology 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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TABLE LEGENDS

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.

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.

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.

FIGURE LEGENDS

Figure 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.

Figure 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.

Figure 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.

Figure 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.

Figure 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.

Figure 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.

Table 1.

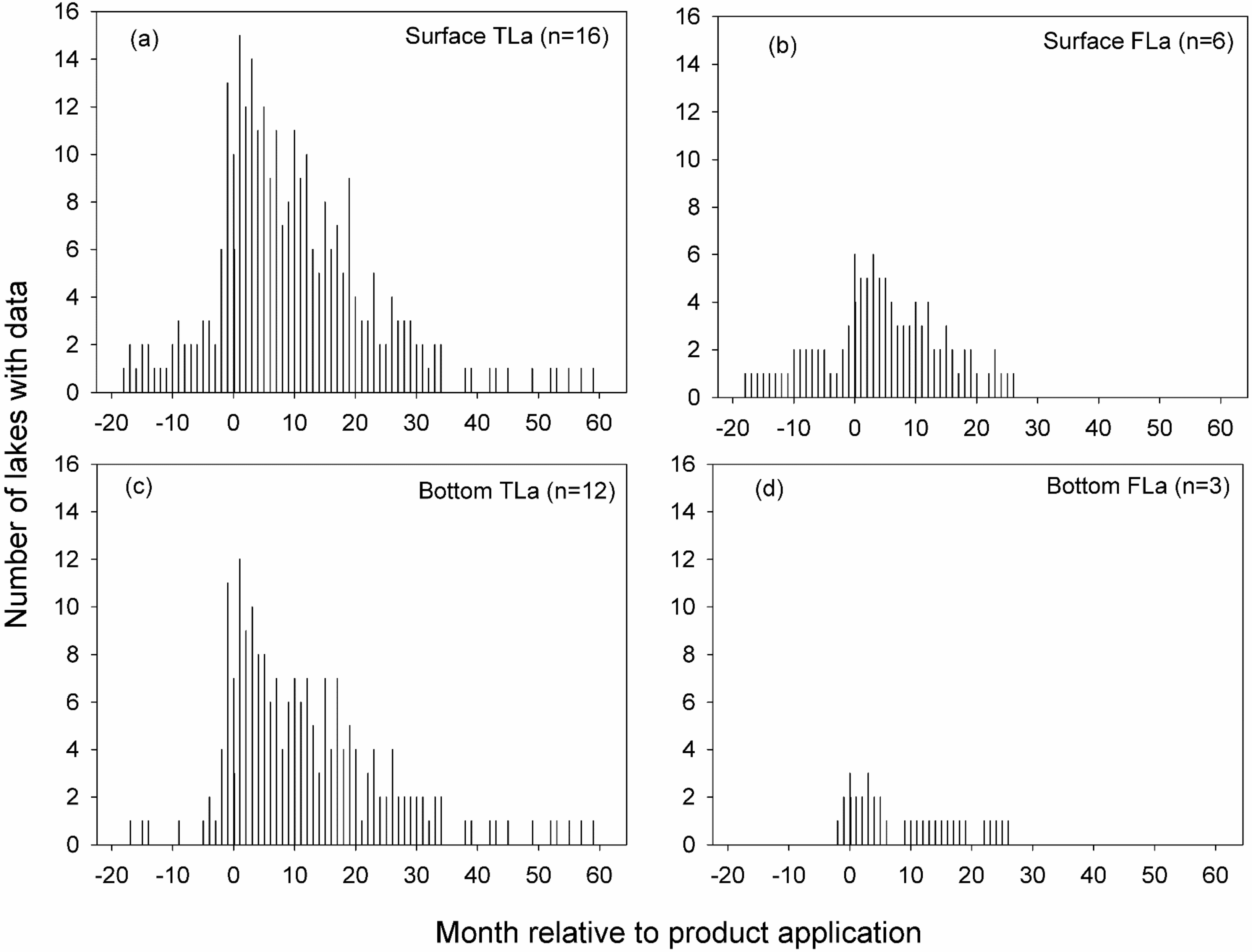
Test organism	Reported stressor	EC50 (mg L^{-1})	NOEC (mg L^{-1})	Test duration	Reference
Zooplankton					
Daphnia carinata	FLa	0.04-1.18		48 hour	Barry and Meehan, 2000
Daphnia magna	FLa	23		48 hour	Sneller et al., 2000
Ceriodaphnia dubia	FLa	5.00	2.60	48 hour	Stauber and Binet, 2000
Ceriodaphnia dubia	FLa	0.08		48 hour	Stauber, 2000
Daphnia magna	Phoslock®	871-1557	100-500	5 day	Lürling and Tolman, 2010
Daphnia magna	Phoslock®	>50000		48 hours	Martin and Hickey, 2004
Daphnia magna	Phoslock®	4900		48 hours	Watson-Leung, 2008
Ceriodaphnia dubia	Phoslock®	>50		48 hour	Ecotox, 2008
Ceriodaphnia dubia	Phoslock®	>1		7 day	Ecotox, 2008
Brachionus calyciflorus	Phoslock®	154	100	48 hours	Van Oosterhout and Lürling, 2012
Fish					
Melanotaenia duboulayi	FLa	<600		96 hour	Stauber and Binet, 2000
Onocrhynchus mykiss	Phoslock®	>13600		48 hours	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

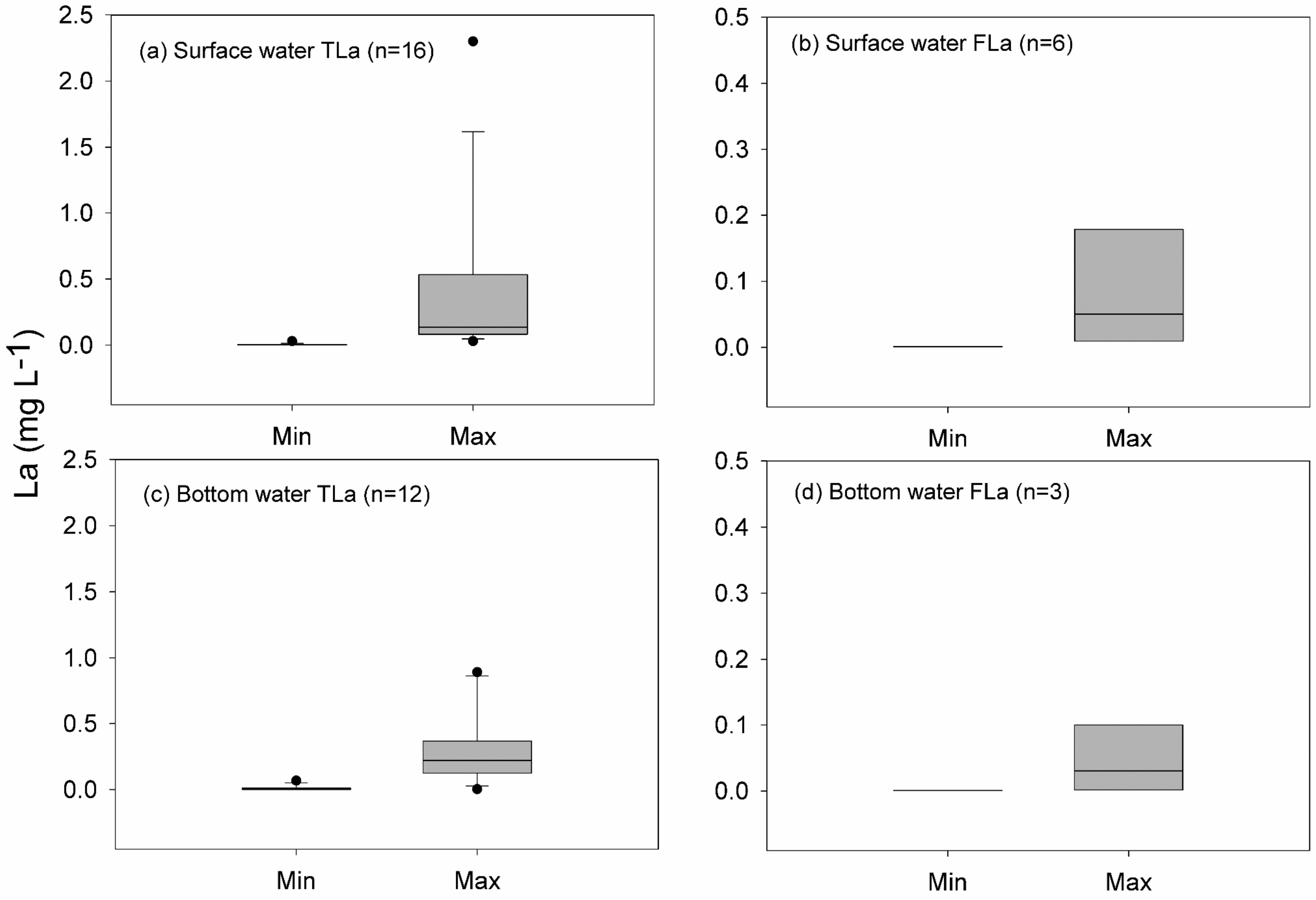
Table 2.

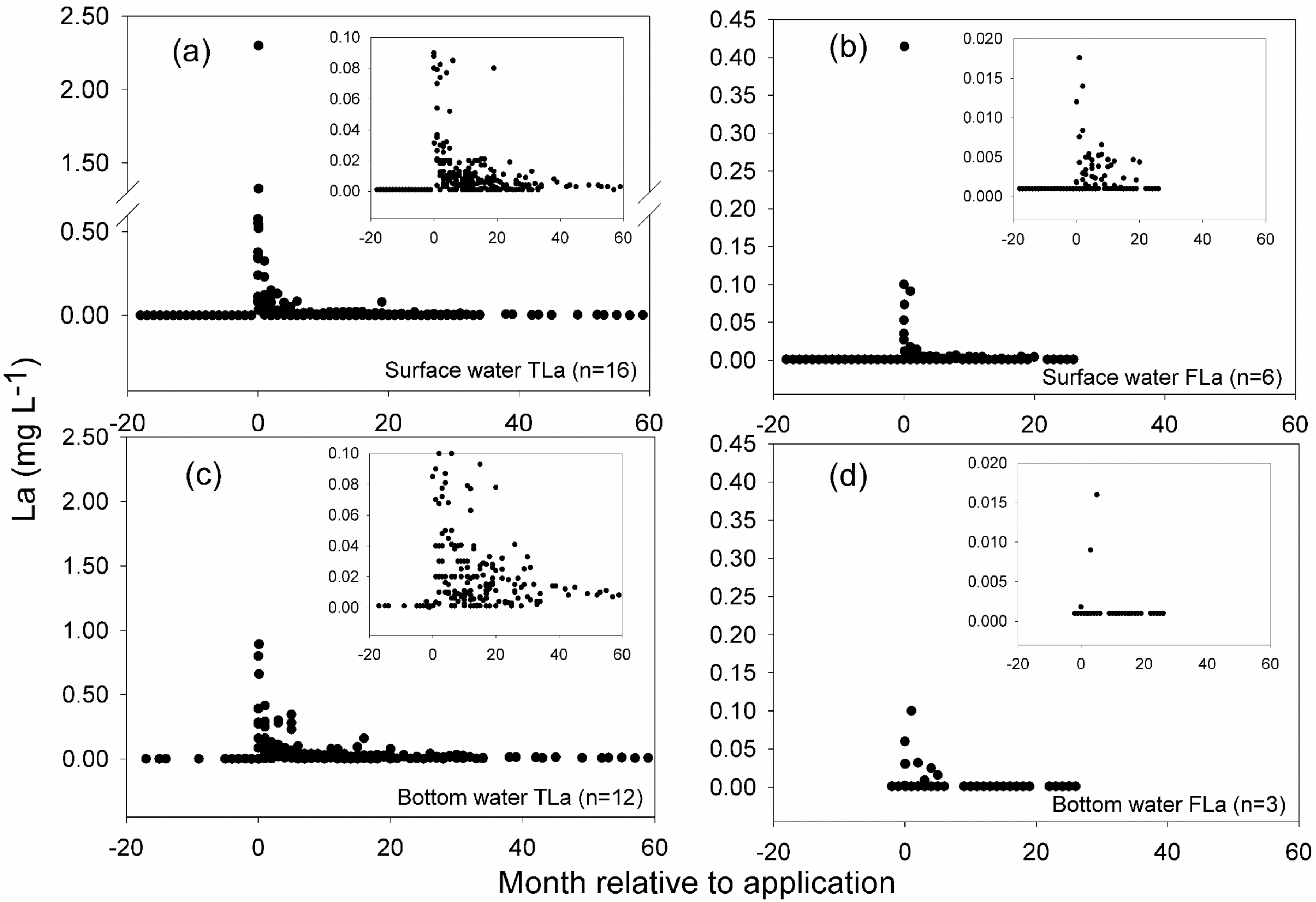
Lake Name	Country	S.A.	Mean	Max	Fetch	Sample location (TLa//FLa)		Date and mass	Phoslock® Load
		(ha)	depth (m)	depth (m)	(km)	Surface?	Bottom?	applied (tonnes)	(tonnes ha^{-1} / mg L^{-1})
Clatto Reservoir[1,2]	UK	9.0	2.8	7.0	0.4	Y/Y	N/N	04/03/2009 (24.0)	2.67/96.97
Loch Flemington[1,2]	UK	15.7	1.0	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

Table 3.

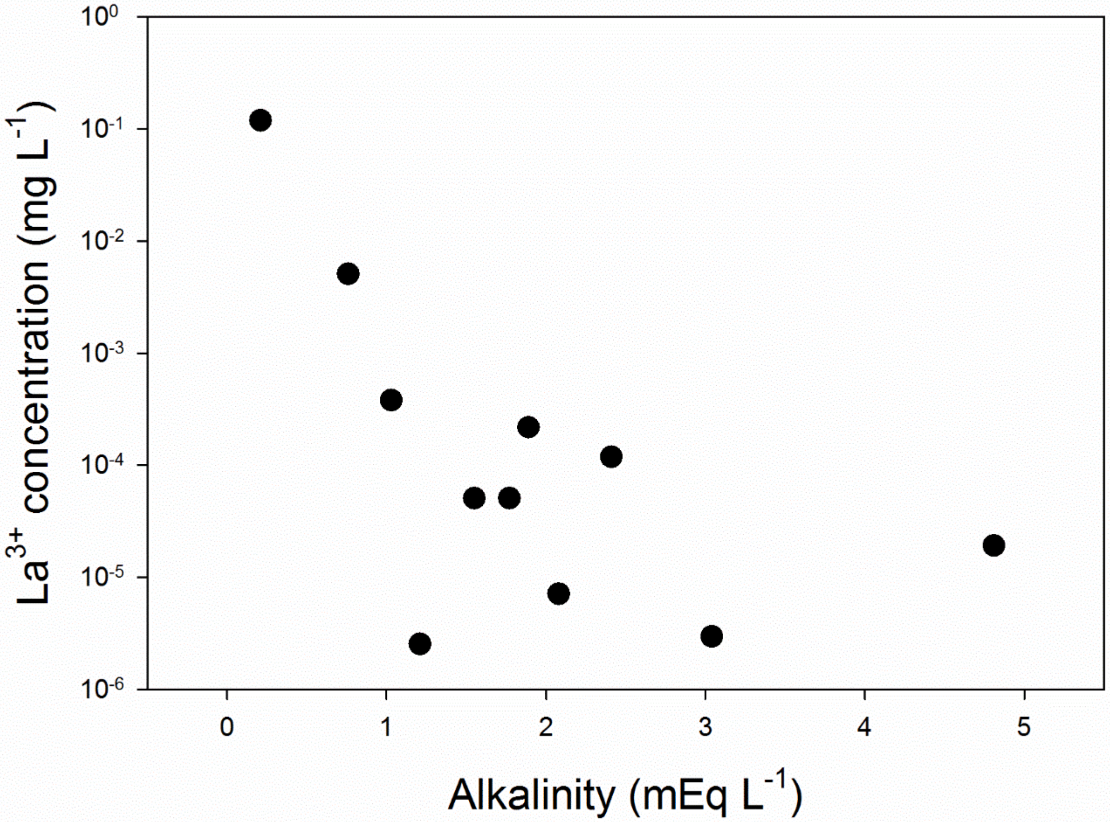
Response variable	**r^2_{adj}**	**N = …**	**P value**	**Deviance (%)**	**Recovery time (months)**	**End point value (mg L^{-1})**
Surface water TLa concentration	0.50	237	< 0.001	64.5	8	0.007
Surface water FLa concentration	0.31	77	< 0.001	67.8	3	0.004
Bottom water TLa concentration	0.32	178	< 0.001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

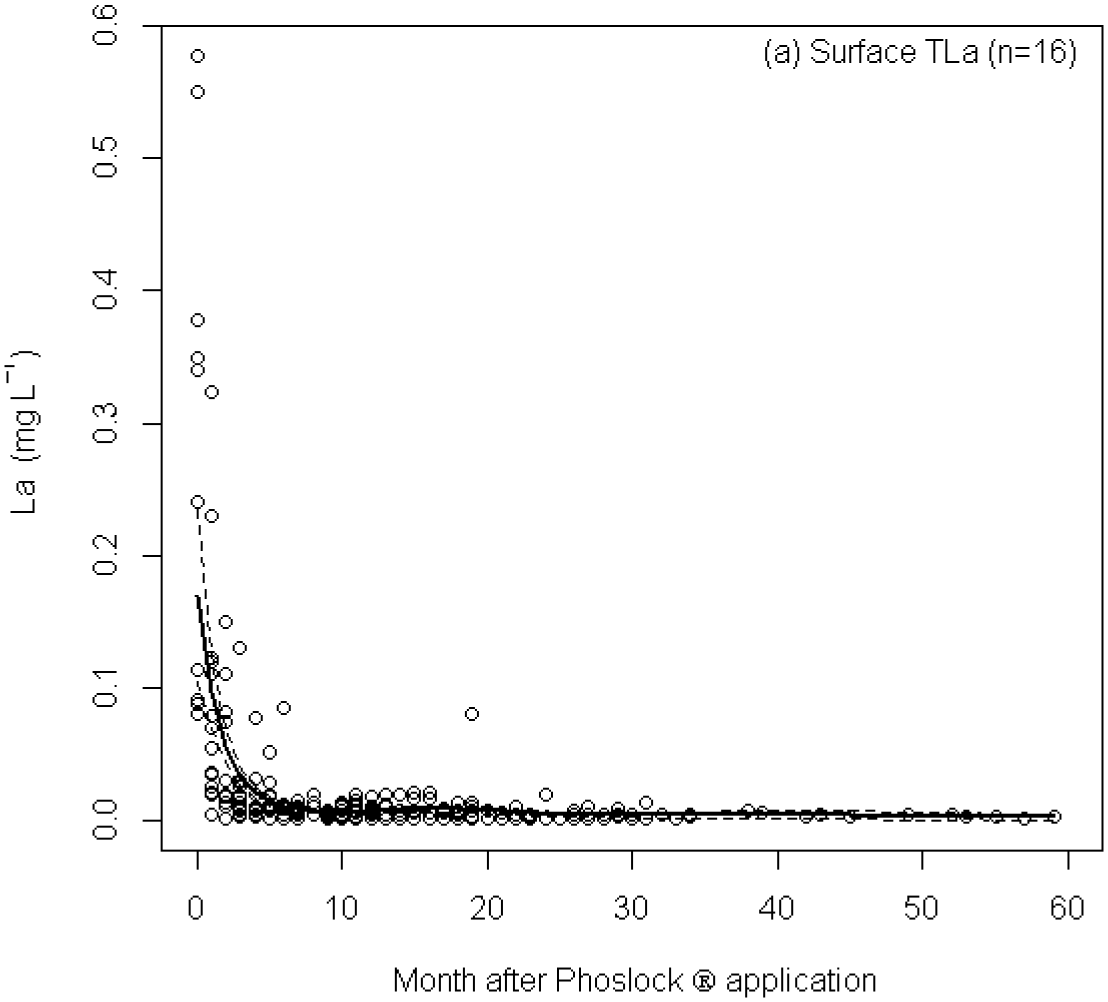

(a)
Surface TLa (n=16)
(b)
Surface FLa (n=6)
(c)
Bottom TLa (n=12)
(d)
Bottom FLa (n=3)
Number of lakes with data
Month relative to product application
0
2
4
6
8
10
12
14
16
-20
-10
0
10
20
30
40
50
60

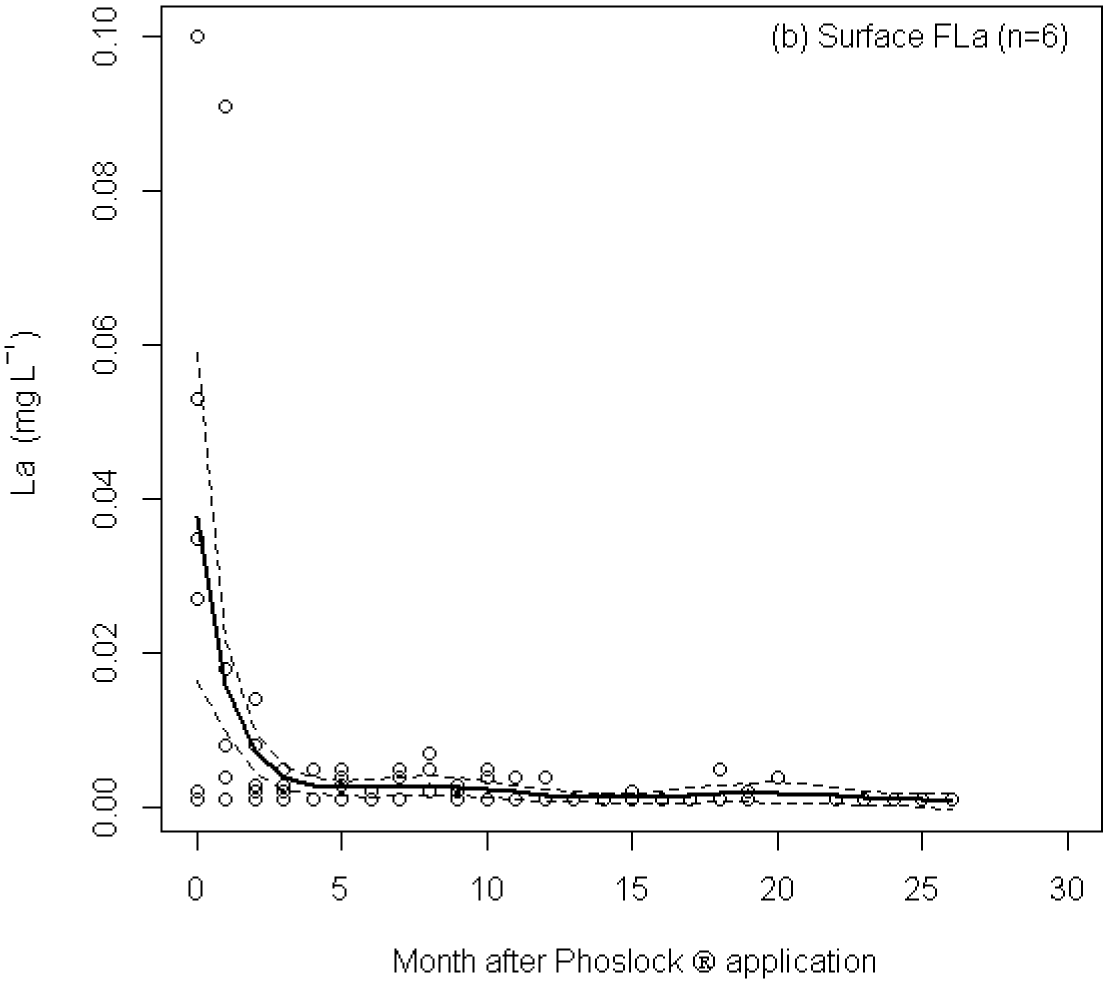

La (mg L-1)
(a) Surface water TLa (n=16)
(b) Surface water FLa (n=6)
(c) Bottom water TLa (n=12)
(d) Bottom water FLa (n=3)
2.5
2.0
1.5
1.0
0.5
0.0
0.5
0.4
0.3
0.2
0.1
0.0
Min
Max

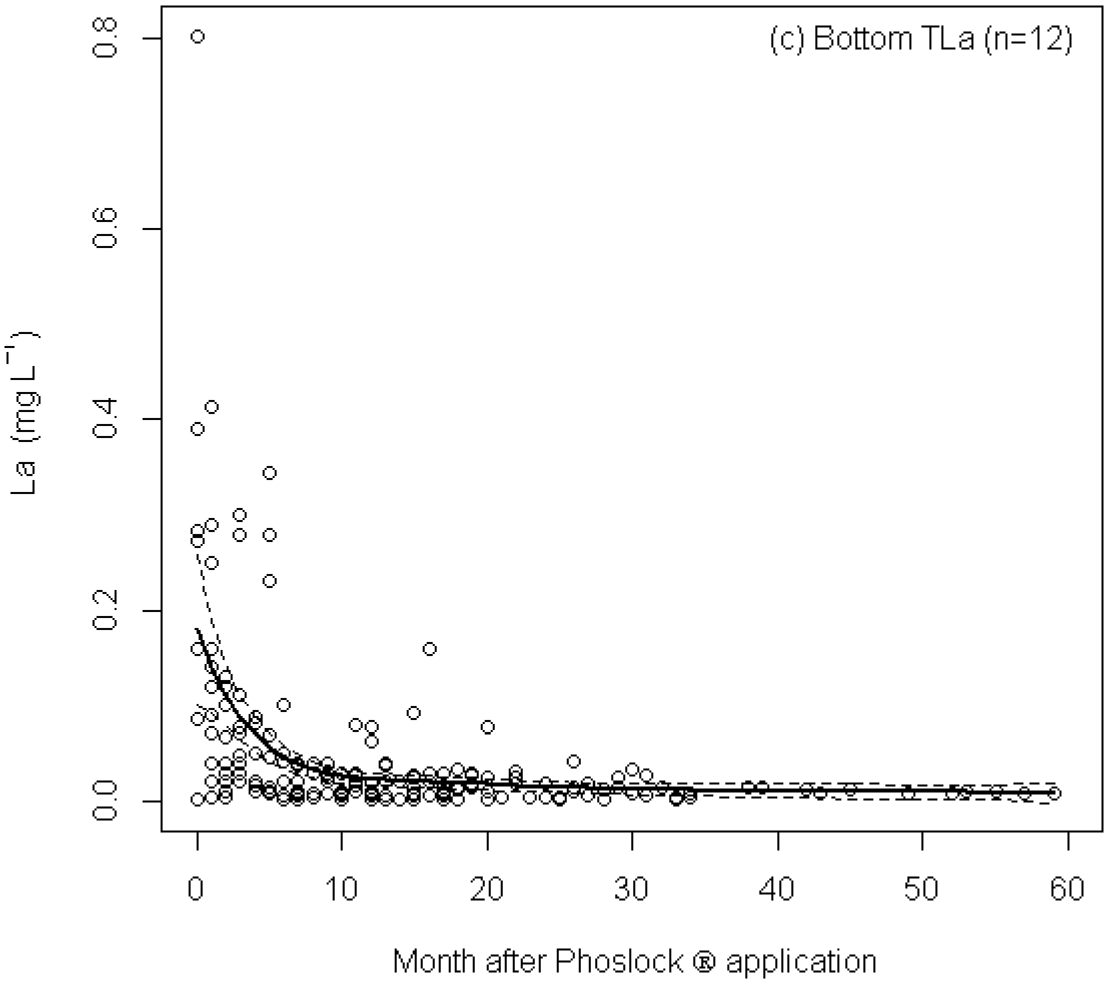


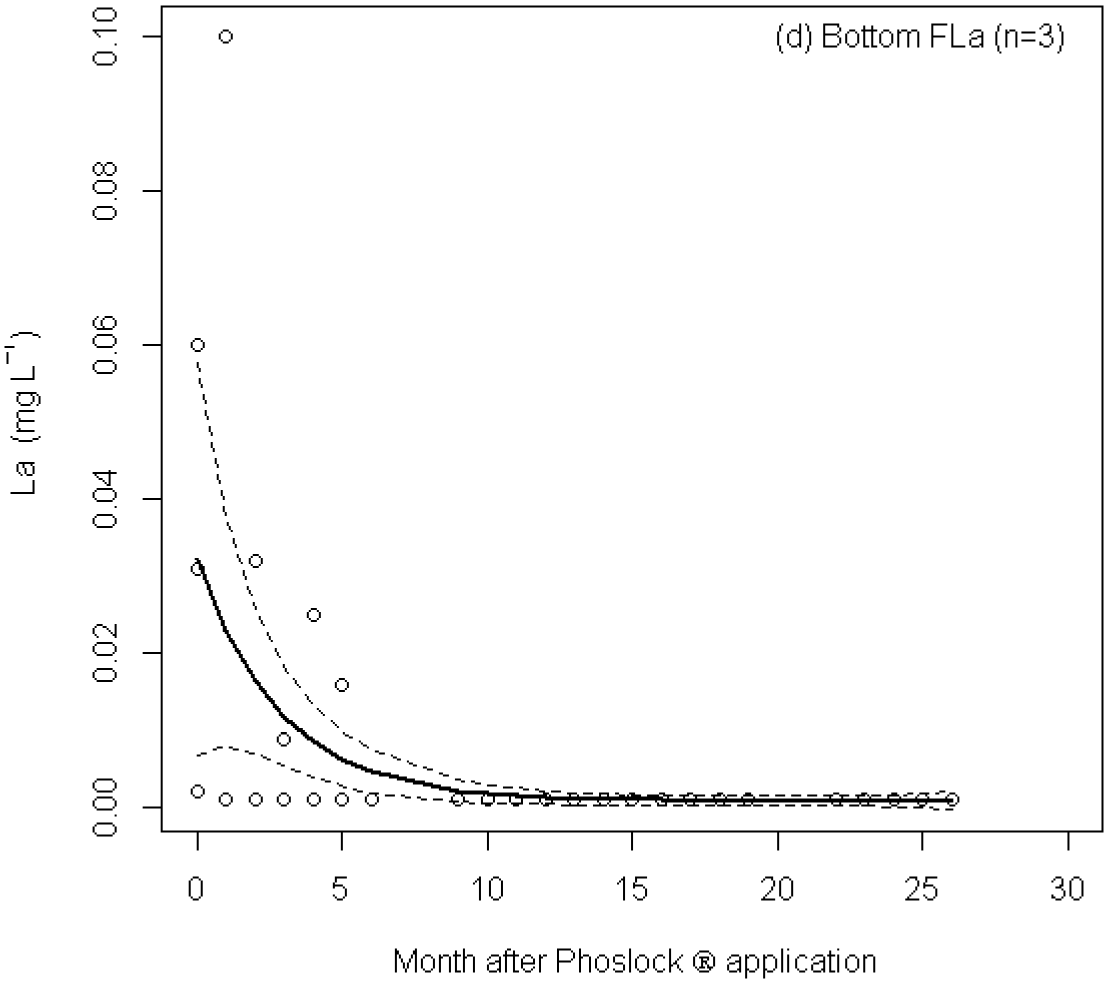
(a)
Surface water TLa (n=16)
(b)
Surface water FLa (n=6)
(c)
Bottom water TLa (n=12)
(d)
Bottom water FLa (n=3)
La (mg L-1)
Month relative to application
2.50
2.00
1.50
1.00
0.50
0.00
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.08
0.06
0.04
0.02
0.020
0.015
0.010
0.005
0.000
-20
0
20
40
60

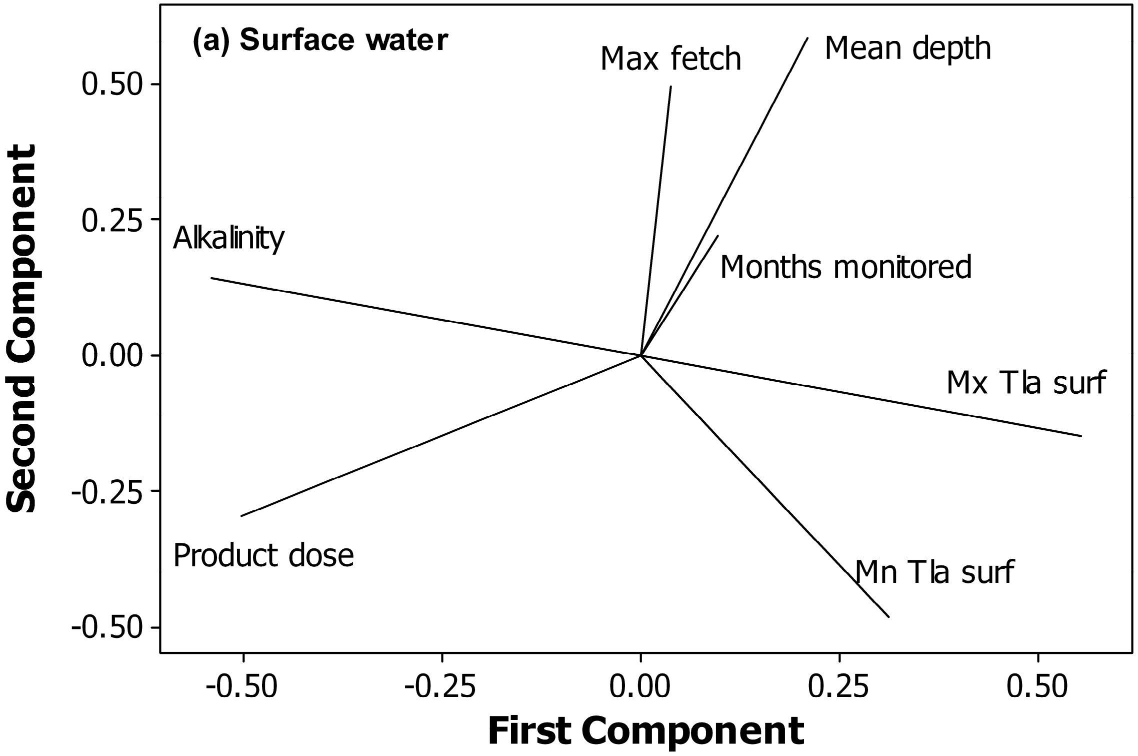

La3+ concentration (mg L-1)
10^0
10^-1
10^-2
10^-3
10^-4
10^-5
10^-6
0
1
2
3
4
5
Alkalinity (mEq L-1)

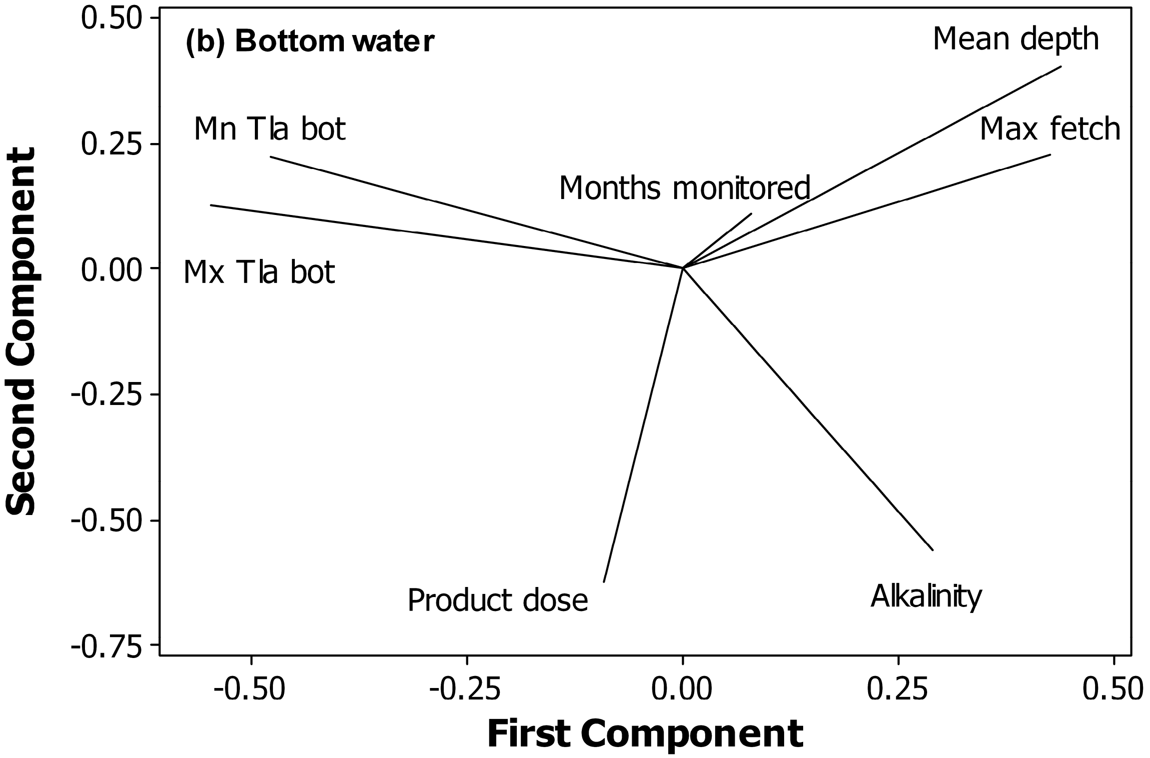

(a) Surface TLa (n=16)
La (mg L^{-1})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
10
20
30
40
50
60
Month after Phoslock ® application


(b) Surface FLa (n=6)
La (mg L⁻¹)
0.00
0.02
0.04
0.06
0.08
0.10
0
5
10
15
20
25
30
Month after Phoslock ® application


(c) Bottom TLa (n=12)
La (mg L^{-1})
0.0
0.2
0.4
0.6
0.8
0
10
20
30
40
50
60
Month after Phoslock ® application


(d) Bottom FLa (n=3)
La (mg L⁻¹)
0.00
0.02
0.04
0.06
0.08
0.10
0
5
10
15
20
25
30
Month after Phoslock ® application


(a) Surface water
Max fetch
Mean depth
Alkalinity
Months monitored
Mx Tla surf
Product dose
Mn Tla surf
0.50
0.25
0.00
-0.25
-0.50
-0.50
-0.25
0.00
0.25
0.50
Second Component
First Component


(b) Bottom water
Mean depth
Max fetch
Mn Tla bot
Mx Tla bot
Months monitored
Product dose
Alkalinity
0.50
0.25
0.00
-0.25
-0.50
-0.75
-0.50
-0.25
0.00
0.25
0.50
First Component
Second Component