

Phoslock Environmental Technologies



Phoslock - an Overview

Introduction

Phoslock is a unique lake management tool which improves ecological structure and function in waterbodies.

Phoslock is a modified clay product, consisting of lanthanum (5%) and bentonite (95%) and was developed in the 1990s by the Australian Government's Commonwealth Scientific and Industrial Research Organization (CSIRO) to improve water quality. Lanthanum is a rare earth element which binds strongly to phosphate, making it a valuable tool in the control of phosphorus pollution in waterbodies.

Phoslock is manufactured through an ion exchange process, whereby lanthanum ions displace sodium and calcium ions within the bentonite matrix and are embedded within the clay layers. The binding of phosphate to lanthanum results in the formation of a non-toxic, naturally occurring mineral (Rhabdophane) that becomes an inert component of the sediments.

Phoslock significantly reduces available phosphorous concentrations in water and sediments and improves water quality.



Phoslock has been extensively tested by regulators and scientific institutions worldwide and is produced according to strict quality control guidelines, having attained National Sanitation Foundation certification (ANSI/NSF 60) for use in potable water supplies and multiple ISO accreditations (ISO – 9001:2015, ISO – 1400:2015 and ISO – 18001:2007).

Over the past 20 years, Phoslock has been applied to more than 300 waterbodies, including lakes, reservoirs, impounded rivers, ponds and brackish and saline waters and used in more than 20 countries. It has been applied to both heavily impacted recreational waterbodies as well as natural waterbodies with high conservation value which fall under the remit of legislation such as the European Water Framework Directive and the U.S. Clean Waters Act.



Sources of nutrient input

Lakes receive phosphorus from a variety of sources, both external and internal (Figure 1). External sources of phosphorus can include diffuse sources such as agricultural run-off and point sources such as septic tanks. Phosphorus can accumulate in lake sediments in large quantities following decades of nutrient pollution, only to be released when environmental conditions change. Untreated sewage effluent contains very high levels of phosphorus. However, septic tanks and treated sewage from failing sewage treatment works can also discharge phosphorus, so lakes which receive effluent, either directly or indirectly, could have received large amounts of phosphorus. Anthropogenic activities increase the natural rate of nutrient input which is a slow process that usually happens over centuries. Climate change (changes in precipitation, wind, increasing temperatures and increased atmospheric pollution deposition) and increased catchment loading from population growth and land-use change are the main external stressors that can increase the rate of internal phosphorus loading to lakes.

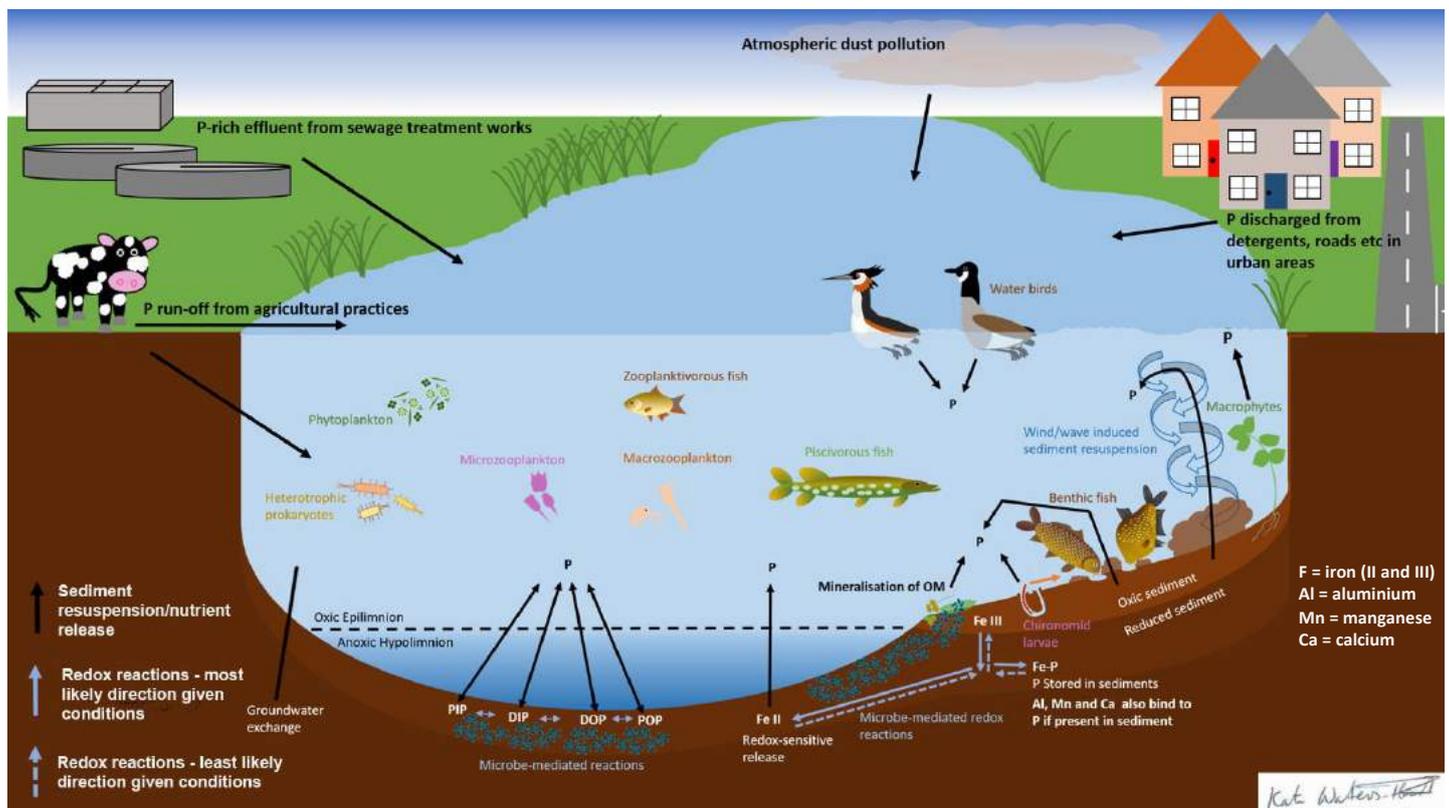


Figure 1. The main sources of phosphorus (P) to a lake, with a focus on both external P sources and internal P load release mechanisms from chemical (redox related reactions during anoxic conditions), biological (bio-turbation (e.g. Chironomidae larvae), disturbance by benthic fish, respiring microbes) and physical (wind/wave action) release processes. The loss of P from a lake system include outflows, through groundwater exchange and sedimentation. P is tied in biomass in the lake (bacteria, phytoplankton, zooplankton, macrophytes, macro-invertebrates (not shown), fish and water birds) and passed through the keychain through predation/bacterivory or released back into the system through biomass degradation and excretion as organic matter (OM). The mineralisation of OM releases dissolved organic P (DOP), dissolved inorganic P (DIP) and particulate organic P (POP).

Phoslock removes excess phosphorus from aquatic systems, thereby improving water quality. Elevated concentrations of phosphorus are the primary cause of undesirable changes to lake ecosystems, including the loss of aquatic plants. Lake ecosystems are able to buffer the effects of increased phosphorus inputs for a while, but eventually the system becomes overloaded and the changes described above typically occur. Even if catchment management reduces external sources of phosphorus entering lakes, it can take several decades, if at all, for the lake to begin to recover due to this legacy.

How does Phoslock work ?

Phoslock works by utilizing the ability of lanthanum to bind with available phosphate as lanthanum removes phosphate very efficiently from aquatic environments (Figure 2). One lanthanum ion will bind one phosphate ion in a molar binding ratio of 1:1. The lanthanum contained within Phoslock reacts with phosphate to form a strong, inert mineral known as Rhabdophane. This is a stable compound which does not dissociate under any of the water quality conditions found naturally in lakes (e.g. fluctuations in pH or anoxic conditions). Reaction rates between lanthanum and phosphate are rapid which results in the quick removal of excess phosphate and the prompt formation of Rhabdophane, which leads to improved water quality conditions (Figure 3).

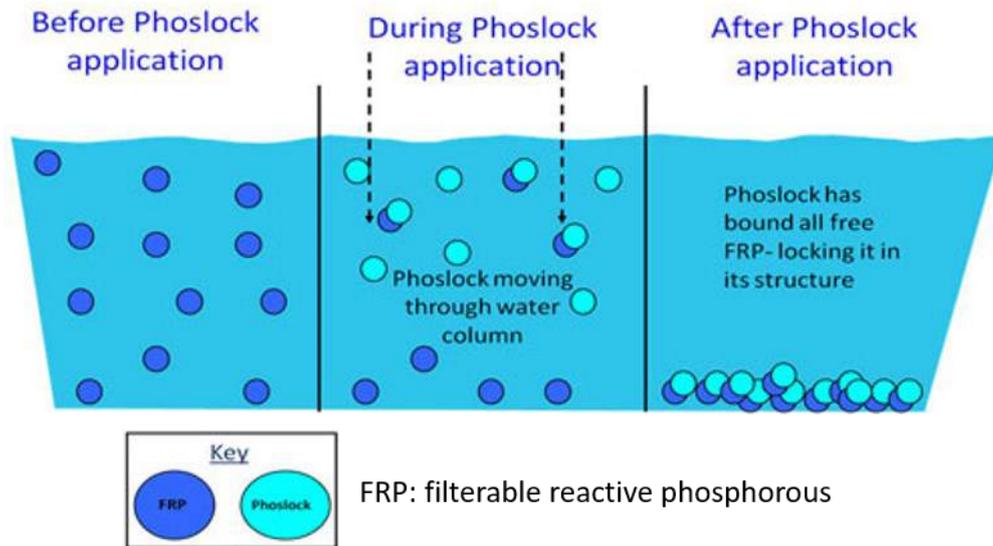
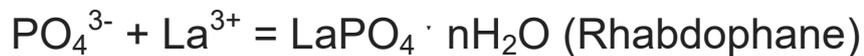


Figure 2. Diagram of Phoslock binding available phosphate

The equation of phosphate binding with La to form Rhabdophane:



One tonne of Phoslock will bind 34 kg of phosphate (11 kg of phosphorus). This occurs over a wide pH range, however the most effective binding occurs between pH 5 – 9. Phosphate is still bound outside of this range but the binding efficiency is slowed if competing oxyanions and hydroxyl ions such as carbonate, hydroxide and humic substances are present. However, the bonds between these substances and La are weaker than those formed with phosphate, and over time, will dissociate and be replaced with Rhabdophane. Phoslock is also efficient at binding phosphate in anoxic waters, meaning that Phoslock can be used not only in shallow aerobic waterbodies, but also in deep stratifying lakes where large amounts of phosphorus are often released from anoxic sediments during summer stratification.



Figure 3. After the application of Phoslock at De Kuil, Netherlands

Phoslock is manufactured and transported in a granule form. On application to waterbodies, granules are mixed with lake water to form a slurry, which is then sprayed over the surface of the waterbody (Figure 4). This enables Phoslock to disperse into many tiny particles which sink slowly through the water column, binding available phosphate as they settle, before forming a thin layer on sediment beds. Settling rates vary according to the chemical composition of the receiving waters but all Phoslock particles typically reach the bed sediments in a matter of days or weeks. Once on the sediment surface, Phoslock forms a fine layer where it continues to bind available phosphate as it is released from the sediments until the lanthanum binding sites are full.

Phoslock does not form an impenetrable physical barrier once it 'caps' the sediments and overtime this layer is worked into the sediment profile through bioturbation by benthic organisms such as chironomid larvae. Rhabdophane remains in-situ and becomes part of the sediment profile which can help consolidate fine and fluid sediments.



Figure 4. Diagram of the Phoslock application process, with Phoslock in its granule form (left), granules being mixed with lake water (middle) and then applied to the surface of a waterbody (right)

Applying Phoslock

Phoslock is generally applied to water bodies as part of a turn-key solution which includes both the supply and application of the product. Applications, especially large-scale applications, are usually planned and undertaken by trained staff from Phoslock Environmental Technologies Ltd., its licensees or approved sub-contractors.

Dosage Calculation

Phoslock dose rates are tailored for each waterbody but are generally based on total phosphorus concentrations in the water column and the amount of “potentially releasable phosphorus” (PRP) in the sediment (Figure 5). PRP in the sediment refers to phosphorus that may be released from the sediment under varying environmental conditions (e.g. under anoxia, at high or low pH and through degradation of organic matter) and an estimation of the PRP load in sediments will enable an assessment to be made as to how much Phoslock needs to be added in order to control sediment phosphorus release. Not all PRP will be released from sediments within one, two or even three years as phosphorus contained in deeper sediments may take many years to diffuse into the overlying water column and organic phosphorus may only become available over a number of years through microbial degradation processes.

A variety of methods can be used to assess the PRP, however the most common method is based on the results of a fractionation procedure (Psenner, 1988; Hupfer, 1995) and the dry weight analysis. Once the percentage of available phosphorus in the sediment has been assessed through Psenner fractionation, an estimation as to which depth of sediment will interact with the overlying water column should also be made in order to determine a suitable sediment capping dosage.

A number of authors have considered this issue and various estimates have been made. Cooke et al., (2005) estimate that most phosphorus release occurs within the top 4 cm while other studies have suggested that a sediment depth of up to 10 cm should be taken into account (Boström et al., 1982). Dosage calculations for most of the projects that have been undertaken with Phoslock worldwide in recent years have been based on the top 4 or 5 cm of sediments. However, in very shallow lakes and lakes with relatively fluid sediments, sediment depths of up to 10 cm have been considered.

Dosage calculation of waterbodies

$WCL + PRP \times \text{lake volume} = \text{lake phosphorous load (kg)}$

WCL = water column total phosphorous load

PRP = phosphorous load potentially released from sediments (usually the top 5cm)

$\text{lake phosphorous load (kg)} \times 100 = \text{Phoslock dose (tonnes) required}$

As an estimate without knowing the specific phosphorous concentrations of a waterbody, for every hectare, 2 tonnes of Phoslock is applied.

Figure 5. How dosages are calculated. If inflow phosphorus concentrations or other external phosphorus inputs (e.g. from water birds) are known, these concentrations are also included in calculating an effective dose.

Application Strategies



Application strategies can be tailored to the particular characteristics of the water body. Global Positioning Satellite (GPS) and depth detection systems are used at all times and higher dosages of Phoslock are sometimes applied to areas of a water body where concentrations of phosphorus in the water or sediment are known to be particularly high.

It is also possible to apply Phoslock either directly onto the surface of the water body or directly into the hypolimnion. The latter approach is recommended when most of the phosphorus in a water body is located either in the sediment or the hypolimnion and when Phoslock drift into the littoral zone of the lake is to be avoided.

Phoslock can be added to a lake as a “one-off” application. In this case, enough Phoslock should be added to bind virtually all of the “potentially available” phosphorus from the lake water and from the sediment. Essentially, the larger the dose (i.e. the more phosphorus removed from the system), the longer and more robust the effect. An alternative to a “one off” dosage of Phoslock could be to add Phoslock in a staged approach. In this scenario, an initial dose would bind phosphorus from the water column and the top 4 cm of sediment and a monitoring programme would be put in place. This would indicate if and when the next dose is required. The timing of any subsequent “top up” applications will depend on the lake, external sources and the size of the first dose, but, if required, could be two or more years after the first dose. Applications of Phoslock in this manner would be “additive”, that is, the improvements from the first application will be built upon by subsequent applications as more and more of the historically accumulated phosphorus is bound. Depending on the size of the first dose, it is also probable that later applications will be significantly smaller than the initial ones.

Application Systems



A number of systems exist for the application of Phoslock. Most comprise a system of motorized coupling pontoons onto which a mixing and application system is mounted. Either steel or modular plastic pontoons such as those in the background graphics can be used.

The product is loaded onto the pontoon system using extended arm forklifts or telescopic loaders. Lake water is pumped through the mixing system and Phoslock is gravity fed through a hopper into the mixer. It is then mixed into a slurry before being dispersed onto the surface of the water body through a spray boom or injected directly into the hypolimnion.

Most application systems require two or three operators. One operator steers the vessel according to a pre-determined course while the other operator(s) feed the product into the mixing and application system. The barge is driven in transects (using GPS and depth sounders) across the lake or reservoir to ensure an even distribution of Phoslock across the surface or in targeted areas.



The binding of phosphate to lanthanum as it travels through the water column results in the formation of a non-toxic mineral (Rhabdophane) that becomes an inert component of the sediments

Large systems comprising up to 6 coupled pontoons are used for large scale applications. These systems can hold up to 12 tonnes of product and a small crane is installed on board (Figure 6) to lift the bulk bags over the hopper through which the product is gravity fed into the mixing system.



Smaller applications can be undertaken using a variety of land-based mix and pump systems (Figure 7). Further details and system specifications can be obtained by sending an email to info@phoslock.eu.



Figure 6. Treatment to a large waterbody using a crane fitted pontoon system



Figure 7. Treatment to a smaller waterbody using a land-based application system

Where has it been used ?

Over the past 15 years, Phoslock has been applied to more than 300 waterbodies worldwide. Pre- and post-treatment monitoring has accompanied most of these treatments and many of the results are now published in peer-reviewed articles in scientific journals. The two case studies described on pages 10— 13 are examples of two contrasting projects. The first, is from a Northern German lake, Behlendorfer See, where external inputs of phosphorus had been largely controlled due to catchment management measures. Here, a single Phoslock treatment has resulted in more than 10 years of improved water quality. The second example (pages 11—12) is from a smaller lake in Central Germany, Bärensee. This lake is an intensively used recreational lake and, as a result, receives continuous inputs of nutrients. Here a strategy of small re-applications every three or four years has been employed in order to maintain low phosphorus concentrations.



Behlendorfer See, Germany

Behlendorfer See (Figure 8) is a 63 ha lake near the city of Lubeck in Germany which is frequently used for various recreational activities. It stratifies thermally during summer months, has a maximum depth of 15 m and an average depth of 6.2 m. For many years, the lake received high loads of nutrients from its predominantly agricultural catchment and the lake gradually “switched” from its natural clear water state to a turbid state. Poor water quality occurred regularly during summer months and as a consequence there was a low diversity of submerged macrophytes. As a result, the lake did not meet the ecological criteria outlined under the European Water Framework Directive.

Figure 8. Behlendorfer See (source—Google Earth)

Despite various measures successfully implemented in the catchment to reduce external phosphorus inputs, the lake failed to recover due to the on-going release of phosphorus from lake sediments (“internal phosphorus loading”). An application of 214 tonnes of Phoslock (marketed as Bentophos in Germany) was undertaken on the lake in December 2009, in order to bind phosphate released from the sediment and improve water quality. The material was applied to a surface area of the lake of approximately 40 ha, which corresponded to the area of the lake which is deeper than 7m. The aim of the application was to remove 550 kg of phosphorus from the water column and 1590 kg of immediately and potentially releasable phosphorus from the upper 5 cm layer of the lake sediments.

Since the application, the lake has been regularly monitored by the regional environmental agency. The monitoring data show that total phosphorus and phosphate concentrations have dropped substantially (Figure 9 and 10). Phosphorus release from the sediment has ceased and the improved water transparency has resulted in increased growth of submerged macrophytes.

Summary of results (Behlendorfer See)

- Rapid phosphorus-binding to lanthanum
- Reductions in in-lake phosphorus concentrations
- Reductions in releasable sediment phosphorus
- Increased macrophyte colonisation depth
- Improved oxygen profile

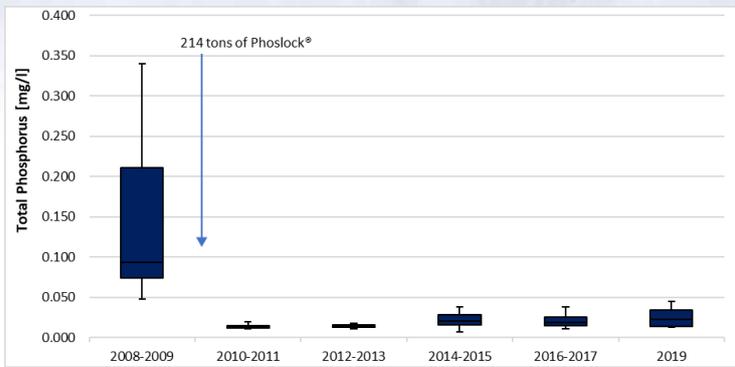


Figure 9. Phosphorus measured in the Behlendorfer See before and after Phoslock application in December 2009 (Source: LLUR)

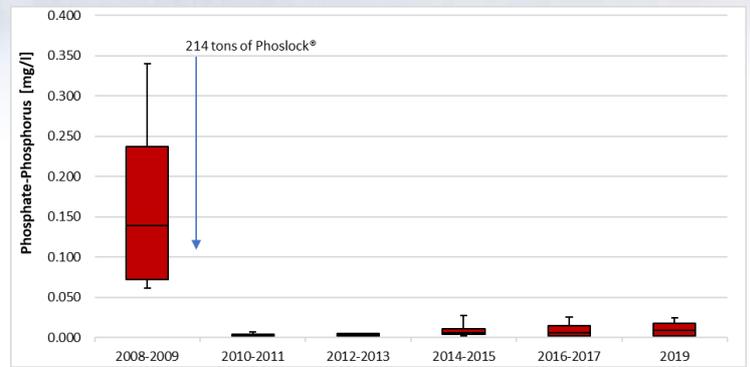
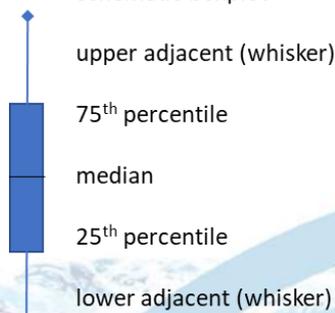


Figure 10. Soluble phosphate-phosphorus measured in the Behlendorfer See before and after Phoslock application in December 2009 (Source: LLUR)

Explanation
Schematic boxplot



Bärensee, Germany

Lake Bärensee is an artificial, shallow, polymictic lake which is located within the largest camping area in the Federal German State of Hessen (Figure 11). It is a very popular lake for swimming and fishing, attracting thousands of visitors during the summer (Figure 12). The lake is surrounded on three sides by camping grounds. It has sandy beaches and is bordered by a forest to the east. Water quality started to deteriorate in the 1990s and very high phosphorus concentrations were measured in the lake by 2004. The lake suffered from periodic swimming bans which severely decreased the recreational value of the lake. The lake was first treated with 11.5 tonnes of Phoslock in 2008 with several smaller applications of Phoslock undertaken in the years since, to immobilize new inputs of phosphorus into the lake from external sources (e.g. swimmers, campsites, etc.).



Figure 11. Lake Bärensee

Figure 12. Swimming area in Lake Bärensee

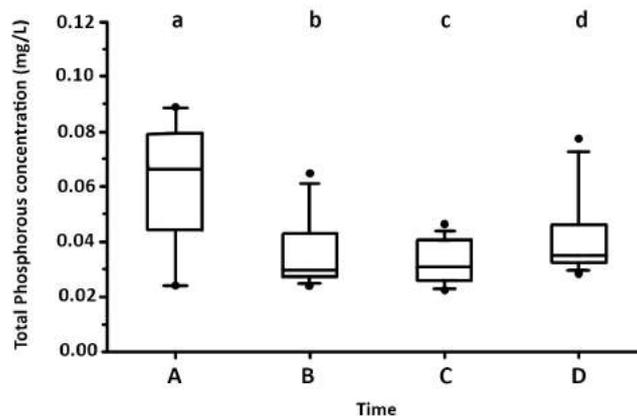


Figure 13. Range of TP among temporal subgroups (A–D). Samples in period A (n = 9) were taken in 2007. B (n = 14) comprises samples from 2008 to June 2010. C (n = 16) covers the period between the 1. and 2. reapplication of LMB in March 2013. Samples in period D (n = 14) were taken after 2. reapplication of LMB up to end of 2015. Groups that do not share the same small letter (a, b, c; above the boxes) are significantly different (Mann–Whitney U-test; $P < 0.05$). Source Epe et al., 2017

Is Phoslock safe for use?

Phoslock has been comprehensively researched within the scientific community over the past 25 years. During this period, a large number of research projects have been undertaken investigating the potential toxicity of Phoslock to both aquatic life and human health. These studies have been conducted across a full range of scales, from laboratory and mesocosm experiments to whole lake studies and have conclusively shown that the use of Phoslock poses negligible risk to aquatic biota. Toxicology is the study of how chemicals interfere with the normal function of a biological system and toxicological assessments of adverse effects are generally based on the use of defined dose descriptors such as EC_{50} (an ecotoxicity dose descriptor defined by the lowest concentration where 50% of test subject species show an effect). The active element in Phoslock, lanthanum, binds very strongly to available phosphorus but could be potentially toxic to some aquatic organisms if it were present in water in its dissolved form (La^{3+} (free lanthanum)). The incorporation of lanthanum into a bentonite carrier overcomes this and prevents any negative impact when lanthanum is applied in the form of Phoslock to fresh waters. Bentonite acts as a lanthanum carrier and has a naturally low toxicity.

Once Phoslock is applied to freshwaters, it forms very small particles and the lanthanum in the water column is analytically determined as total lanthanum (TLa) and filterable lanthanum (FLa). Especially in soft water lakes Phoslock disperses, resulting in very fine non-toxic lanthanum containing particles that can pass through various filter sizes (Reitzel et al., 2017). Reitzel et al., (2017) point out that much of the FLa measured, even after 30 minutes of ultracentrifugation, were still very fine colloids and not truly dissolved lanthanum. Only in lake water, with a combination of very low alkalinity, low phosphate and very high dissolved organic carbon, is the FLa concentration measured in the filtrate after ultracentrifugation probably considered in its dissolved form; likely to be associated with humic substances. Ultracentrifugation is time consuming and costly and the use of lanthanum speciation modelling has been used in many scientific publications to accurately assess if La^{3+} ions could be released from Phoslock following an application. This chemical equilibrium modelling enables lanthanum speciation to be determined prior to Phoslock treatment under the specific physio-chemical conditions of the waterbody. This allows an accurate estimation of dissolved lanthanum cations in the water with respect to the specific water chemistry of the waterbody. This is of particular importance in very soft water lakes with low phosphate and high humic substance concentrations as these are the only conditions when ionic lanthanum could potentially occur following a treatment. However, when Phoslock is applied to lakes with at least moderately low alkalinity, concentrations of dissolved lanthanum can be expected to be very low. It is also important to know that unreacted lanthanum remains within the clay matrix and is not expected to easily diffuse out of the carrier material (Dithmer et al., 2015).

In addition to phosphate, lanthanum also binds other oxyanions (e.g. carbonate). Soft water lakes have lower concentrations of these oxyanions and therefore, if the concentration of phosphate in the water is low, less lanthanum binding activity occurs. Consequently, in low alkalinity, soft water lakes with a high humic substance content in the water, Phoslock dosages should be calculated with care and chemical equilibrium modelling is a suitable tool to ensure that sufficient concentrations of phosphate are present in order to bind any lanthanum cations that could potentially be released from Phoslock under these particular conditions.

Toxicity studies of lanthanum to freshwater biota have been conducted using different forms of lanthanum, including lanthanum chloride, lanthanum nitrate and lanthanum-modified bentonite (Phoslock). These studies have covered a wide range of aquatic biota such as zooplankton, macroinvertebrates, fish, nematodes and macrophytes, but results have varied according to the test stressor used. This variability is the result of the different chemical properties of soluble lanthanum salts compared to Phoslock and it is therefore important for ecotoxicological assays to reflect realistic conditions of an application scenario. Consequently, tests should be conducted with Phoslock itself rather than surrogate substances in order to fully understand toxicity impacts.

Measuring TLa concentrations in the water column is a good way to assess if Phoslock is present post-treatment. Lanthanum is usually bound very quickly to available phosphate and so TLa concentrations decrease in a waterbody over time. The EC₅₀ concentrations of the studies that have used Phoslock as the stressor for assessing toxicity amongst aquatic groups are considerably higher than those ever recorded in systems where Phoslock has been applied.

Lanthanum can bioaccumulate in fish, crayfish, chironomids, macrophytes and waterbirds following applications. In some cases, lanthanum has accumulated for up to five years following a treatment. However, no adverse effects have been reported in any of the peer-reviewed studies that have investigated this.



Humans can also theoretically be exposed to Phoslock through using recreational waterbodies following a Phoslock application. Exposure pathways are most likely through ingestion and dermal contact, caused by swimming or watersport activities and from fish consumption. It should be noted however, that lanthanum carbonate is used for medicinal purposes to treat patients suffering from hyperphosphatemia. Sold under the trade name, Fosrenol[®], lanthanum carbonate is typically administered at doses of between 375 and 3,000 mg/day of elemental lanthanum, usually over many years. Based on an average prescribed dose of 1,500 mg/day (~900 mg lanthanum/day), users of recreational water bodies treated with Phoslock would need to consume at least 380 L of water per day in order to ingest the same quantity of elemental lanthanum as an average Fosrenol[®] dose. This large volume of water is impossible to consume by a person in a day and therefore, an application of Phoslock would never deliver as much lanthanum as a single Fosrenol[®] tablet. The long-term consumption of lanthanum carbonate (10+ years) has shown no adverse safety outcomes amongst patients. Similarly, consumers would need to ingest vast amounts of fish; more than 1,000 kg per day based on the highest flesh lanthanum concentrations recorded in fish to reach the nominally safe recommended therapeutic dose in adults.

In summary, based on the responses of a range of aquatic organisms, the risk of toxicity to aquatic life is low following a Phoslock application to a waterbody. The ingestion of Phoslock treated water directly after an application would pose no risk to human health and similarly eating fish that have accumulated lanthanum would also not pose a risk.

Phoslock versus other chemical measures

A variety of different approaches can be adopted to tackle high nutrient concentrations in waterbodies. Some measures, such as algaecides and biological control measures, are aimed at controlling the symptoms of nutrient enrichment and do nothing to address the underlying high internal nutrient load. Other measures aim to reduce nutrient concentrations to levels which are more typical of unimpacted aquatic systems. These other measures can include, for example, dredging and chemical phosphorus inactivation.

Phoslock is an in-lake solution that specifically targets phosphorus pollution and internal phosphorous load.

More than 140 materials able to bind phosphorus have been identified in the scientific literature. However, the vast majority of these have only been tested in the laboratory and there is a lack of published information about their toxicity, efficiency under differing environmental conditions, longevity and costs. Additionally, many of the materials are not manufactured or produced in commercial quantities.

Commercially available phosphorus-binders include: Phoslock, aluminium sulphate and poly aluminium chloride, ferric chloride and various calcium-based compounds and as well as a number of natural clays and soils. Phoslock has several advantages over these phosphorus-binders (Table 1). For instance, unlike iron and aluminium salts, Phoslock does not impact the pH or conductivity of the water in which it is used. This avoids the need to add additional chemicals to the water (e.g. to buffer the pH) and eliminates any stress to aquatic organisms caused through pH changes. Phoslock binds phosphorus under a wide pH range, under anoxic conditions, in the presence of humic substances and also in saline waters. These are major advantages over natural clays and soils as well as calcium, iron or aluminium compounds. Another advantage is the stable bond between Phoslock and phosphate. Once Phoslock binds to phosphate, the phosphate it has adsorbed will not be released under anoxic conditions or when the pH of the water changes. Other phosphorus-binders available commercially such as, iron and aluminium salts are far more likely to release the phosphorus adsorbed when pH changes (e.g. aluminium) or when anoxic conditions develop (e.g. iron salts). Unlike aluminum salts, Phoslock does not crystallize. Phoslock will not lose its binding capacity over time and has the capacity to increase sediment stability. Phosphate bound to lanthanum cannot be released as a result of resuspension events caused by wind or waves or bioturbation.

Phoslock versus other chemical measures

Table 1. The advantages of using Phoslock over other phosphorus binding commercial products.

| Phoslock | Aluminium salts | Iron salts |
|---|--|---|
| Effective between pH 5 and 9 | Effective between pH 6 and 8 | Effective between pH 5 and 8 (depending on the salt used) |
| Effective under anoxic conditions | Effective under anoxic conditions | Not effective under anoxic conditions |
| Does not affect water pH and conductivity | Affects water pH and conductivity | Affects water pH and conductivity |
| Increases sediment stability | Does not affect the sediment stability and can easily resuspend | No studies have been done on the effect of sediment stability |
| No need to be applied with a buffer | Might need to be applied with a buffer | Might need to be applied with a buffer |
| Phosphate adsorbed will not be released under anoxic conditions or within pH 4 - 12 | Phosphate adsorbed will not be released under anoxic conditions or within pH 6 - 9 | Phosphate adsorbed will be released under anoxic conditions |
| Binding capacity does not decrease with time | Binding capacity decreases with time | Binding capacity may decrease with time |
| Does not have coagulant properties | Has coagulant properties | Has coagulant properties |

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